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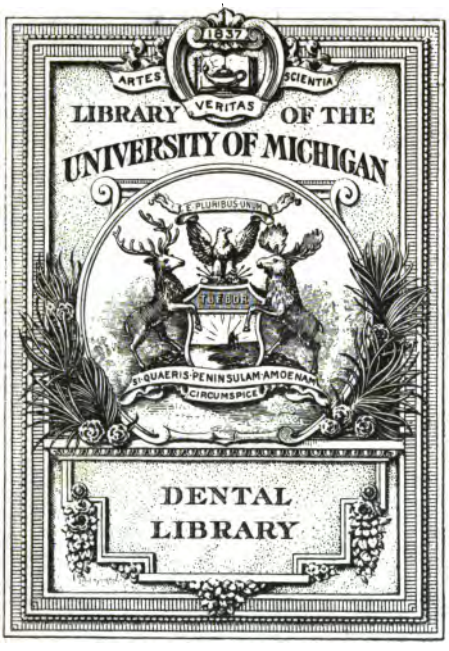
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# METALLOGRAPHY

## AN INTRODUCTION TO THE STUDY OF THE STRUCTURE OF METALS, CHIEFLY BY THE AID OF THE MICROSCOPE

BY

ARTHUR H. HIORNS

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# PREFACE.

THE demand for practical instruction in all branches of a subject in our Technical Schools is increasing, and the introduction of experimental work is so moulding the character of the teaching, that the teacher must keep himself conversant with the new developments that are constantly arising in consequence of the progress of scientific knowledge.

In accordance with these views the author has made a special study of the intimate structure of metals during the last few years, and found great pleasure in following the researches of those who may be rightly termed the pioneers in metallography, such as Sorby, Martens, Osmond, Stead, Roberts-Austen, Arnold, Andrews, and several others, whose patient and laborious efforts have brought to light such a precious fund of knowledge that many of the hitherto unsolved problems have now received a satisfactory explanation.

As far as the author is aware of, no book on the subject has before been published in the English language; and as metallography is yet in its infancy, it is not sufficiently developed to permit of its being placed on a strictly logical scientific basis. This is therefore only an attempt to lay the principles of the subject before students and workers who are interested in the properties and applications of metals, and to offer a series of original illustrations which it is hoped will assist in making the meaning clearer.

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Although the photographs are the best the author has been able to produce with the apparatus at his disposal, they give but an imperfect idea of the delicate structures which are revealed by direct vision through the microscope, even when a cheap instrument is employed; for to get a proper idea of any section a number of views of the different parts are requisite, and these should be examined with different powers, from the pocket lens up to the highest possible magnifications of the microscope. For the purposes of this book, most of the photographs have been taken with an inch and a quarter-inch objectives, giving an amplification of 120 and 220 diameters respectively.

The introductory chapter gives a brief account of the history and development of metallography, including a statement of the nature of alloys as generally recognised by eminent metallurgists, apart from microscopic considerations.

As the minute structure of metals can only be correctly investigated on a perfectly polished specimen, free from scratches, the subject of polishing naturally claims an important place, and such appliances as can be used by the humblest worker, as well as more elaborate and labour-saving machinery, are briefly enumerated, especially those methods adopted by the great masters of the subject. Closely connected with this are the operations of etching, oxidising, and colouring, which are most important aids to structure revelation.

A concise description of a suitable microscope with appliances for illuminating the sections is given. The subject of Photo-Micrography is also dealt with, and simple directions given for photographing the prepared specimens, together with the kind of plates used by the author and the most suitable paper for printing.

The structures of the different varieties of iron, steel, and cast iron are described in considerable detail, for the reason that they form the most comprehensive and

important of metallic materials, and have been more completely investigated than those of other metals. The other metals included in the present work are chiefly those of industrial importance, and consist of Copper; Copper-Tin alloys and special Bronzes; Brass; German Silver; Gold; Silver; and Miscellaneous Alloys.

A Glossary of terms used in Metallography is added as a help to the student in grasping the meaning of technical words used in the text, especially as different investigators have found it necessary to coin some new words to express previously unknown phenomena that they have observed.

The author wishes to record his great indebtedness to Mr. J. E. Stead, who most generously placed all his published researches at his disposal, and volunteered the loan of any of his original photographs. The author further records the valuable assistance he has received from Mr. C. R. Clark in executing the photographs; from Mr. J. H. Stansbie in reading the proof-sheets; and from the various original papers duly acknowledged in the separate pages.

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6. Austenite.
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9. ,, ,, (Long.).
10. White Cast Iron.
11. ,, + 2 % Manganese (cooled quickly).
12. ,, + 2 % Manganese (cooled slowly).
13. Wrought Iron (Trans.).
14. ,, ,, (Long.).
15. Pure Iron.
16. Dead Soft Iron.
17. Mild Steel, 0·15 % C.
18. Copper with 1 % Bismuth.
19. Steel, 0·11 % C annealed at 700° C.
20. ,, 0·3 % C.
21. ,, 0·6 % C.
22. ,, 0·9 % C.
23. ,, ,, hardened.
24. Steel, 1·2 % C.
25. ,, ,, hardened.
26. ,, 1·8 % C.
27. ,, ,, hardened.
28. Silicon Steel, 4·5 % Si.
29. Cemented Steel.
30. ,, ,, hardened.
31. ,, ,, 0·8 % C,
32. Ferro-Manganese.
33. Silicon Pig Iron.
34. Ferro-Tungsten,
35. Ferro-Chrome.
36. Ferro-Nickel.
37. Slip Bands.
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44. Copper containing Silicon.
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47. ,, ,, Bismuth.
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49. ,, ,, Aluminium.

FIG.
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81. ,, ,, Antimony.
82. ,, ,, Aluminium.
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85. Silver containing Arsenic.
86. ,, ,, Antimony.
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94. ,, 40 % + Antimony, 60 %.
95. Copper, 10 % + Antimony, 90 %.
96. Copper, 85 % + Antimony, 15 %.

# CHAPTER I.

## INTRODUCTION.

§ 1. The study of the internal structure of metals by means of the microscope practically originated in the year 1864 with Dr. Sorby of Sheffield, who was the first to publish a paper on the peculiar microscopic structure of iron and steel. The idea apparently lay dormant until the year 1878, when Professor Martens in Germany contributed a paper on the "Microscopic Structure of Iron and Steel." He has since published the results of his various investigations and may now be considered one of the greatest authorities on the subject. Other workers, notably Messrs. Osmond and Werth in France, began to perceive the great possibilities of the new method and devoted close attention to it, with characteristic thoroughness and energy. This recognition of the importance and practical application of microscopic research brought back Dr. Sorby to the field with additional contributions on micro-metallography. In 1882 he delivered a lecture on the subject in the Firth College, and in 1886 to the Iron and Steel Institute, on the "Application of very High Powers to the Study of the Microscopical Structure of Steel." In the following year a similar paper was also contributed. In the meantime the subject was vigorously pursued in other

countries, for we find a paper by J. C. Bayles on the "Microscopic Analysis of the Structure of Iron and Steel," in the *Transactions of the American Institute of Mining Engineers for* 1883, and again in 1885 by F. Lynwood Garrison. In 1885 Messrs. Osmond and Werth contributed a paper on the "Cellular Structure of Iron and Steel," and in the same year Dr. Wedding read a paper to the Iron and Steel Institute on the "Properties of Malleable Iron, deduced from its Microscopic Structure." For the next ten years metallography was closely studied in France, Germany, and America, while during all this period extremely little notice of this work was taken by the British technical press, and as Mr. J. E. Stead remarks, "No person in the whole of Great Britain appeared to consider the matter of sufficient importance to notice, until Professor J. O. Arnold commenced working at it about 10 or 12 years ago. Thus it will be seen that the infant science, born in Sheffield, has been for many years neglected in the Mother Country and has been fostered abroad."[1] It is pleasing to have to record that this state of things no longer exists, and that Mr. Stead stands in the front rank of active and enthusiastic workers. He, as well as Professor Arnold have already added immensely to our knowledge by their papers, not only on the structure of iron and steel, but of other metals and their interesting alloys.

The microscope is making its appearance in many of our large works, and industrial chemists and experts of different kinds are eager to embrace this new means of investigation. It must be clearly recognised at the outset that microscopic examination is not intended, nor ever will replace chemical analysis or mechanical testing of metals. Its function is to add additional information of a kind which other methods are incapable of yielding. Thus, in steel, ordinary chemical analysis will indicate

[1] Paper on "Study of Micro-Metallography," *Cleveland Inst. of Engineers*, 1895.

the total quantity of carbon, combined and free, but will not reveal the presence of definite mineral constituents, such as ferrite, cementite, pearlite, martensite, and the manner in which they are associated in the steel. Again, in an alloy, such as brass, chemical analysis will give the percentage of copper and zinc, but will not tell us how many different compounds or alloys exist in the main alloy, or whether any free metal is present. It will not reveal the internal structure, crystalline or otherwise, which so materially modifies the physical properties, and alone will not prove the presence or absence of an eutectic mixture. It is true that some of these properties may be discovered by other means, but even then the microscope is a valuable aid in confirming results brought out by other physical methods. To quote again from Mr. Stead, "In microscopic research we have a simple and inexpensive method by which a mind may be made to think and a brain to act, and although it may be many years before sufficient practical data and knowledge are obtained to class micro-metallography as an exact science and a constant practical guide, in the meantime such work will tend to raise the employé from the unthinking machine to the intelligent workman."

Professor Roberts-Austen states that microscopic metallography has not been developed from petrography, but is closely connected with and is a natural extension of the study of meteoric irons. It must be remembered however that Dr. Sorby recorded observations upon the microscopic examination of thin sections of rocks in 1858, in a paper on the microscopic structure of crystals, indicating the origin of minerals and rocks. A similar paper was also communicated in 1867 by Mr. David Forbes, Secretary of the Iron and Steel Institute. These observations gave birth to the science of petrography. As already stated, Dr. Sorby, in his first paper on the peculiar structure of polished sections of iron and steel,

pointed out the fact that metallic bodies bear a striking resemblance to rocks. He afterwards devoted himself largely to the complete development of the method of examining sections of opaque bodies under the highest magnifying powers, and the application of this method to different products of iron and steel. Professor Martens seems to have devoted his attention at first to the elucidation of general laws dealing with fractures, fissures, blow-holes, and crystallisation in metals, and M. Osmond claims for the labours of the latter experimenter all the characters of complete originality. In 1880 the use of the microscope was introduced into the Le Creusot Works and the investigations of Messrs. Osmond and Werth have been continued since that time along the path indicated by Dr. Sorby. This will probably become historical, being the first attempt to transfer the study of metallography from the scientific laboratory to the works laboratory as an indispensable auxiliary to chemical analysis and physical tests.

Metallography bears a close analogy to petrography, or study of rocks, and the use of similar technical terms in both cases may be employed. In the development of a new branch of science the nomenclature is liable to become very involved, especially when it is being pursued in different countries and under different conditions. The Council of the Iron and Steel Institute have therefore appointed a committee, including English, American, French, German, and Austrian representatives, to consider the matter and to ascertain whether it would be possible to take steps to make the terminology less complicated and more precise.

In considering the history of a rock it is necessary to bear in mind that two more or less distinct questions are involved: (1) the origin of the minerals of which the rock is composed; (2) the origin of the rock itself. In some cases there is an intimate connection between the origin of the rock and that of the minerals which

enter into its composition. In some cases the minerals have crystallised *in situ*, and in other cases the origin of the minerals is distinct from that of the rock. Now, just as a rock is made up of distinct compounds, termed minerals, so an alloy or impure metal is generally composed of two or more distinct bodies, each having a composition differing from that of the whole mass. These subsidiary alloys, having a defined constitution and in many cases a characteristic structure, have also definite freezing points, so that they appear to have a separate existence, although their action is limited by being engulphed in the general mass. These bodies therefore exert an influence on the properties of the main alloy, and in many cases this influence is the dominating one. Now, in the case of impure metals and alloys, the subsidiary alloys are the analogues of minerals in rocks, but they are always formed *in situ*, and therefore bear an intimate relation to the main alloy, of which they are the offspring. Further, a rock when cooled very slowly from a molten magma, affords opportunities for minerals to form, to crystallise and become more and more separate, the length of time determining the size of the crystals, but when the molten rock is cooled very rapidly it assumes a glassy and amorphous structure. Very much the same kind of thing occurs in the rate of cooling of alloys. Seeing then that the analogy is so close, it will be very convenient to borrow the name of *mineral* to distinguish these subsidiary alloys and to use similar technical terms to those used by the mineralogist and geologist in describing the structures of metals and alloys.

If a metal, or an alloy of metals, naturally assumes a crystalline structure, the molecules which are the component parts of matter probably also assume a definite shape, and arrange themselves in contact with each other so as to form larger crystals of the same shape, and the slower and more uninterrupted the action the larger will

the crystals grow, and the more symmetrically will they arrange themselves in relation to each other.[1] If a metal is submitted to pressure not only will the individual crystals be distorted but the orderly arrangement of the whole mass will be disturbed, and when the pressure is carried on to a certain extent the metal will become so weak as to be easily fractured by a slight additional force; in other words, the metal becomes rigid and brittle, a state of unstable equilibrium being brought about. Now, in all probability the natural crystalline condition is the stable condition, and any deviation from this may be said to be unnatural. In such a case the molecules are ever tending to pass back again to the normal and more highly crystalline state, which is perfectly effected by remelting, and often in a great measure by annealing.

Under suitable conditions, the growth of a crystal (due to the continued deposition of the minute crystals in close contact) increases and becomes more compact, and any foreign matter which separates the smaller crystals is squeezed out into the larger channels between the faces of the larger crystals, but may be arrested by pressure or quick cooling. If this view be correct, the tendency in the molecules of a distorted metal to change is more effective at a high than at a low temperature, but even at the ordinary temperature the change may occur if sufficient time be allowed, and it is a well-recognised fact that metals subjected to stress or vibration do in time become crystalline and break, because in a state of transition the metal is obviously weak, and the stress prevents the molecules from assuming that symmetrical arrangement which they would do if the mass were in a state of rest.

A metal which naturally forms large crystals, such as zinc, is generally weaker than one whose crystalline

[1] See Paper by A. Wingham, *Jour. Iron and Steel Inst.*, Sep., 1901.

structure is small, especially when much impurity is present, because it is more prone to continue the crystalline growth when cold, and as the impurities tend to arrange themselves along the faces and prevent perfect contact, fracture commonly occurs along such planes of weakness. Messrs. Ewing and Rosenhain have shown [1] that the cleavage planes of a crystal are not the result of the deposition of layer upon layer, for when the crystals of a piece of lead are strained under compression, beyond the elastic limit, they grow with arms and branches thrown out, and produce spaces between them which become filled up at a later stage and form the face of the crystal. Such fern-like growths are observed in other metals.

With regard to alloys, including steel and cast-iron, which may be termed alloys of iron and carbon, etc., there is a close analogy to that class of indefinite compounds, termed solutions. They may be considered as solidified solutions of metals which contain definite compounds, or metals in an excess of one of the constituent metals. Matthiessen regards it as probable that the condition of an alloy of two metals in the liquid state may be either that of: (1) A solution of one metal in another; (2) chemical combination; (3) mechanical mixture; (4) a solution or mixture of two or of all of the above, and that similar differences may obtain as to its condition in the solid state. He also classifies the solid alloys, composed of two metals, according to their chemical nature.

1. Solidified solutions of one metal in another: lead-tin, cadmium-tin, zinc-tin, zinc-cadmium and lead-cadmium alloys.

2. Solidified solutions of one metal in the allotropic modification of another: lead-bismuth, tin-bismuth, tin-copper, zinc-copper, lead-silver, and tin-silver alloys.

3. Solidified solutions of allotropic modifications of

[1] *Proc. Roy. Soc.*, vol. 65, p. 85.

the metals in each other: bismuth-gold, bismuth-silver, palladium-silver, platinum-silver, gold-copper, and gold-silver alloys.

4. Chemical compounds of the alloys corresponding to $Sn_5Au$, $Sn_2Au$, and $Au_2Sn$.

5. Solidified solutions of chemical compounds in each other: the alloys intermediate between those corresponding to the above formulæ.

6. Mechanical mixtures of solidified solutions of one metal in another: alloys of lead and zinc containing more than 1·2 per cent. of lead, or 1·6 per cent. of zinc.

7. Mechanical mixtures of solidified solutions of one metal in the allotropic modification of another: alloys of zinc and bismuth containing more than 14 per cent. zinc, or more than 24 per cent. bismuth.

8. Mechanical mixtures of solidified solutions of allotropic modifications of the two metals in each other: most of the silver-copper alloys.[1]

As before stated, an alloy may be compared to a rock, which contains different constituents, all of which may be united in the liquid condition but separate on cooling, forming two or more alloys of different densities and of different fusibilities. Or many solid alloys, when heated, release certain of their constituents that have different freezing points from the remainder. In fact, a cooling mass of mixed metals often behaves like water containing suspended matter does in freezing, when the ice first formed rejects the foreign matter; and so the portion of the alloy which first solidifies rejects certain other portions of the constituent metals. Thus a mixture of lead, antimony, and copper poured into a cylindrical mould, allowed to cool, and then broken, will show that while the copper and antimony have united the lead has been rejected, and driven to the centre of the mass. A mixture of lead and zinc separates in a similar way. Silver and copper alloys

[1] *British Association*, 1863.

behave in a similar manner, but in any mixture of fused silver and copper, one particular alloy of silver and copper is formed, that is driven inwards or outwards according to whether copper or silver is in excess. This is termed liquation.

Levol has shown that, in cooling alloys of lead with gold and silver, if the latter are present in small quantities they are driven towards the centre of the solidifying mass. Gold of high standard does not, like silver, show any tendency of the constituents to undergo liquation. It is well known that in gold-platinum alloys certain portions of the constituents separate, and become concentrated, either in the centre or in the external portions of the solidifying mass.

Iron and steel exhibit a marked tendency to undergo liquation when slowly cooled. Lencauchez[1] heated fragments of pig-iron to a temperature of 940° C. for 100 hours, and found that a number of spherical grains had extruded, which on analysis were found to contain 4 to 6 per cent. phosphorus, whereas the original pig-iron contained only 1·9 per cent. By applying severe pressure to partly solidified cast-iron Mr. Stead caused the molten interior, into which much phosphorus had penetrated, to burst the tender walls and gush out. This ejected matter contained 6·84 per cent. of phosphorus, while the cast-iron treated contained only 1·53 per cent.

The causes of the separation of certain constituents of steel is attributed by Howe[2] to the struggle between crystallising force and surface tension, aided by gravity; on the one hand tending towards differentiation, and on the other towards diffusion. As the temperature sinks towards the freezing point the surface tension increases, the different constituents tend less powerfully to diffuse among each other, and more to draw apart in drops. Further, as the complex molten

[1] *Mém. Soc. Ing. Civils.*, 1887. [2] *Metallurgy of Steel*, p. 207.

mass cools past the freezing point of a certain potentially present compound, this compound tends to form, to solidify, to crystallise, to expel the more fusible residue, in the same way as a salt in crystallising expels the mother liquor, which is gradually driven towards the last freezing region.

Dr. Guthrie gave considerable attention to this subject some years ago, and came to the conclusion that certain alloys in cooling behave as a cooling mass of granite would; clear molten granite in cooling would throw off "atomically definite" bodies, leaving behind a fluid mass, which is not definite in composition, as the quartz and felspar solidify before the mica. The same thing takes place in cooling fused mixed metals; for when a mixture of lead and bismuth or bismuth and tin cools, a certain alloy of the metals falls out, and the most fusible alloy of the series is left, which Guthrie calls the *eutectic* alloy. It is the most fusible alloy of the series, but the proportions between the constituent metals are not atomic proportions; and Guthrie says, "that the preconceived notion that the alloy of minimum temperature of fusion must have its constituents in simple atomic proportions, and that it must be a chemical compound, seems to have misled previous investigators; but that certain metals may, and do unite with one another in small multiples of their combining weights may be conceded; the constitution of eutectic alloys is not in the ratio of a simple multiple of the chemical equivalents of the constituents, but their composition is not on that account less fixed, nor are their properties the less definite."[1]

The intervention of a third metallic solvent to the two constituents of an alloy which do not naturally mix often causes their assimilation by destroying the eutectic. Until recent years the initial point of solidification was the only one considered, but it is necessary to know

[1] *Phil. Mag.*, June, 1884, p. 462.

what subsidiary eutectic points may be present, as the action of impurities is very marked in connection with them. In some cases the foreign bodies remain in the mass, partly or wholly, as solidified solutions, the impurities being probably dissociated into their atoms in both the solid and the liquid mass. With regard to brasses, Roberts-Austen has shown that they have more than one freezing point, and that the subsidiary freezing points represent eutectic alloys. These alloys were separated by squeezing away the fluid portions in a press. The brass under examination was placed in a steel cylinder fitted with loose plungers, and the whole put between the jaws of a hydraulic press. The cylinder was then gradually heated, and the temperature at any period measured by means of the Le Chatelier pyrometer. At a certain definite temperature part of the alloy will liquefy, and can be squeezed out between the plungers and the wall of the cylinder. The temperature was carefully noted at which any extrusions took place, and the various samples were then analysed.[1]

When an alloy of two metals yields neither definite combinations nor isomorphous mixtures there is only one eutectic, as in lead-tin alloys. When two metals yield one or more definite combinations we get two or more eutectics, as in copper-tin alloys. When two metals form isomorphous mixtures there is no eutectic. This will explain the phenomena of liquation. At the moment when solidification commences there is deposited either a pure metal or a definite compound, and this tends to change the composition of the remaining liquid portion. If the crystalline structure of an alloy appears most often on the fractured surface, or, if it is easy to develop by polishing and etching, it is not a case of eutectic alloys, or isomorphous mixtures, as the crystals of these alloys are of extreme fineness and give to the fractured surface an appearance similar to that of glass.

[1] *Institute of Mechan. Engineers*, 1897.

The effect of heat on an alloy containing an eutectic is to increase the influence of the latter, and in the case of a crystalline metal the eutectic would attack the crystals by penetrating their points of most recent formation, causing the sharp outlines of the larger crystals to become rounded. The effect of compression is to restrict the amplitude of vibration of the molecules and make them more potent, and the eutectic would act on the crystals with greater vigour. Further, the lower the melting point of any foreign element which forms an eutectic with a metal, the lower will be the melting point of that eutectic. Also, as a rule, the greater the number of impurities in a metal the lower will be the melting points of the eutectics. Then the lower the melting point of an eutectic the more favourable will the conditions be for producing a large crystalline structure and the more brittle will the metal become. Hence phosphorus is much more injurious to iron than silicon, as it produces a lower melting eutectic.[1]

[1] Wingham, *Iron and Steel Inst.*, September, 1901.

# CHAPTER II.

## POLISHING AND ETCHING.

§ 2. For exact examination of the structure of metals it is absolutely necessary to have the surface polished free from scratches, as well as perfectly flat, if high powers are to be used, since scratches and other imperfections tend to mask the real structure and convey an altogether erroneous impression as to the character of the components. Now, it might appear that polishing was the easiest and simplest part of the whole process, but experience soon teaches the operator that it requires considerable skill and judgment to perform the finishing touches and remove the last faint marks. Too great care cannot be exercised in properly preparing the polishing blocks, especially the finer ones used for finishing; even a little bit of grit or dirt accidentally falling on the surface may produce an ugly scratch while the finishing touches are being given to a section which has perhaps taken hours to prepare. Different workers employ different methods, but the main principle is the same in all cases; and it will be useful, therefore, to know what plans are pursued by the great pioneers of the subject.

§ 3. **1. Dr. Sorby's Method.**[1]—This great operator first selects a suitable piece of metal, cut from the main

[1] *Iron and Steel Inst.*, No. 1, 1887, p. 255.

mass in a given direction by means of a circular saw. The sections are about half an inch square and one-tenth of an inch thick. One side is then ground flat and fixed on to a small glass plate with hard Canada balsam, so as to form a convenient means of polishing the upper surface, which is to be subsequently examined. This may be conveniently done by placing the glass on an iron or copper plate, heated underneath by a Bunsen's burner or spirit lamp. A bit of hard Canada balsam is then just melted on the glass and the section of metal firmly pressed on. It is then removed and allowed to remain under pressure until it is perfectly set. It is necessary to impress the operator with the importance of using hard or dry balsam in cementing the section to the glass; otherwise failure is sure to ensue. The surface of the section is now rubbed on coarse emery paper, first in one direction, then in a direction at right angles, until the marks are in one direction and the marks previously made by rubbing in the former direction are completely obliterated. This operation is repeated on finer and finer emery paper, finishing with the very finest. It was found, however, that in many cases no good results could be obtained by polishing with rouge directly after using the fine emery, because the surface was so much modified by the scratching; this surface was, therefore, ground off by using fine-grained water-of-Ayr stone and water until all trace of scratches was removed. It was then polished on wet cloth stretched on a piece of wood, using the finest grained crocus, and, lastly, the very best and finest washed rouge, so as to obtain a beautiful polish, almost free from microscopic scratches, without any of the disturbance caused by a forced polish. Sometimes the constituents are of very different degrees of hardness and are rubbed down unequally, which in many cases affords valuable information. In many cases it may be desirable to have all the constituents cut through on precisely the same

level, and the surface of the hard portions made flat and not rounded on the edges. This may be accomplished by polishing dry with rouge on a piece of parchment, laid over a sheet of glass. Some of Dr. Sorby's preparations were polished dry on parchment with rouge, without being acted upon afterwards by acid. In this case the polishing is continued until the structure is brought out to perfection.

Dr. Sorby remarks: "As a general rule, in the early part of my enquiries I developed the structure of sections polished wet by means of extremely diluted nitric acid. The time necessary to develop the structures varied very much. It is well not to dry the specimen but to examine it in water in a glass trough, and, when the result seems satisfactory, to well wash the slide in slightly alkaline water and dry it quickly with a soft handkerchief."

§ 4. **Professor Martens' Method.**[1]—1. The samples are cut into sections of about one to two millimetres. Brittle sections are split by a blow. In each case the sample is taken perpendicular and parallel to the chief directions. The plates, several of them together, are then cemented to a slab of glass or metal with a cement made of equal parts of beeswax and resin. In this case it is necessary that all the sections on the slab should be at the same level. This is done by turning in a lathe, or, in the case of very hard specimens, by grinding. For grinding and fine grinding, emery or crushed quartz is used, and, for polishing, fine quartz sand, oilstone, and polishing rouge.

Prof. Martens says: "As beds (grinding plates) I use glass or metal plates; as polishing beds I use plates of glass or pitch, and but seldom soft ones, such as leather, indiarubber, etc. Pitch plates are made from

[1] "Introd. to Study of Micro-Metallography," by J. E. Stead, *Cleveland Inst., Eng.*, 1895.

pure soft pitch, with a little resin added, by pouring the melted mixture out upon glass plates. In polishing, the chief thing is cleanly, tidy work, carried out in systematic sequence. The kind of 'bed' of grinding and of polishing powder must be selected according to the softness of the metal to be handled, which can only be gained by experience. The time needed to produce a specimen is entirely dependent upon circumstances and experience. At first it takes days to get an imperfect result; afterwards it is possible to do the same in a few hours. Steel specimens of about one square centimetre surface, when ten to twenty are done at once, can eventually be finished off in one day; with special arrangements, even still more."

In preparing the different grades of powder for grinding and polishing, the following plan was pursued: "Pear-shaped vessels, some 2·5 litres and some of 0·5 litre contents, are used, and in them the grinding powders are stirred up with water. The coarse grains settle quicker and collect at the pointed bottom of the flask. The material is divided into grades of fineness according to the time required to settle; at the end of each time limit the water and suspended matter are syphoned off into a fresh flask and allowed to settle there for several minutes, the suspended matter being again syphoned off, and so on. By a systematic grading in this manner is obtained material of two, three, or more sizes of particles. For the finer grades half-litre flasks are used, and the powder is suspended in alcohol or ether.

"When the section is polished it must be separated from its holder and from the cement that adheres to it. The latter is first done mechanically, and finally by treating with alcohol and ether. The section is considered clean when, on removing from the ether and allowing the ether to evaporate, no rim appears on the polished surface. If this cleansing is not properly done,

then, on subsequent warming of the section (for fastening to the object-holder), the residual cement wells up out of the interstices and forms coloured puffed-up ridges to the pores, and gives very deceptive appearances under the microscope.

"Surfaces polished in soft beds, on account of the varying hardness of the constituents of the section, show the 'joinings,' that is, the structure of the preparation, more or less clearly, and the coarser structures may be examined under low magnifying powers in this condition; but in order to obtain an insight into the finer structures the surfaces must be polished on a hard polishing bed (pitch bed). The polished surfaces may be then etched or coloured to bring the components into view. Surfaces polished in soft beds also become usually more defined when etched or coloured."

§ 5. **Professor Arnold's Method.**—The sections, after being cut to size, are finished if possible with a dead smooth file, and the file-marks subsequently removed on the finest emery cloth, stretched on a hardwood board. The remaining operations are conducted on materials stretched by means of taper rings on cast-iron blocks, and of the following nature: No. 1 block contains the finest emery cloth from which the coarse emery has been removed by rubbing first with a marble slab, and secondly, with a piece of smooth hard steel about one inch in diameter. On No. 2 block is stretched thick black unribbed cloth, charged with oil and the finest emery knife-polish. On No. 3 block is a piece of finest wash-leather, slightly charged, dry, with the best jeweller's rouge. The average time occupied in each stage is: On emery cloth, five minutes, and on Nos. 1, 2, and 3 blocks, about ten minutes each.

§ 6. **M. Osmond's Method.**—This indefatigable worker has brought to bear on the subject of micro-metallography such an amount of skill and scientific insight

that his remarks on the subject naturally carry the greatest weight, especially as his descriptions are marked with the utmost clearness and conspicuity. As methods of obtaining suitable sections have been already explained in the methods of the previous workers, they need not be again repeated here. M. Osmond seems to despair of getting sections sufficiently smooth by the aid of the professional polisher, by means of revolving emery wheels, bobs, and mops; he is reduced to the necessity of obtaining suitable sections, free from scratches, by the tedious and laborious operation of rubbing by hand. He therefore adopted a series of emery papers placed on glass. The papers are prepared as follows: "I buy the 'potful' termed 120 minutes, that is to say, that took 120 minutes to settle. I carefully mix this with water, and collect the deposits formed at certain intervals in precipitating glasses. The following is an example of division of 100 parts:

| | | |
|---|---|---|
| Amount deposited in | less than one minute, | 16 |
| ,, ,, | from one to two minutes, | 13 |
| ,, ,, | from two to five minutes, | 8 |
| ,, ,, | from five to ten minutes, | 6 |
| ,, ,, | from ten to twenty minutes, | 14 |
| ,, ,, | from twenty to forty minutes, | 8 |
| ,, ,, | from forty to sixty minutes, | 11 |
| ,, not deposited in sixty minutes, | | 24 |
| | | 100 |

The powders thus obtained are dried, mixed with a paste of albumen, which is used for the preparation of sensitised paper, and spread on paper of the best quality."[1] As a rule, four grades of paper of increasing fineness are used, marked Nos. 1, 2, 3, and 4 respectively. No. 1 is used to remove file marks. Over No. 2 the section is rubbed 100 times backwards and forwards, then over No. 3 an equal number of times, and lastly over No. 4 about 500 times. After the emery papers the sample is

[1] *Bull. de la Soc. d'Encouragement*, 113, 480-516.

polished with rouge, spread on a piece of parchment, stretched over a slab of oak. A little water is used with the rouge, and the sample of metal is rubbed backwards and forwards about 500 times. Commercial rouges are not all of a suitable quality. Those marked "for steel" are too hard and coarse for untempered steels; those marked "for gold" are better, but it is advisable to wash them before use. These products change with time, perhaps on account of a molecular change, which in an oxide of iron is not improbable. In short, it is best to prepare one's own rouge, carefully avoiding the presence of any hard impurity, by carefully calcining sulphate of iron and separating the finest parts by washing. It may be also made from oxalate of iron. Instead of parchment the rouge may be applied to cloth having a fine nap and stretched double over the polishing block.

§ 7. **Polishing in Bas-Relief.**—When a complex substance is polished, its different constituents tend to wear away unequally, according to their specific properties and absolute dimensions, and it is possible by placing it in convenient positions to show the structure by the unequal relief of its components. To obtain this result it is necessary to polish the section on a bed elastic enough to wear away the little protuberances as they are formed, and delicate enough to bring out the finest details. Osmond found parchment the best for this purpose, stretched on a piece of perfectly smooth wood. A small quantity of rouge, damped with water, is then rubbed in with the finger, and the excess washed off by water, so as to keep only the very finest particles, which have penetrated into the pores of the parchment. On this prepared surface the metal to be polished is rubbed, adding a little water from time to time. The hard constituents appear much more quickly in relief as their relative resistence to wear is greater and their dimensions larger. However, the finest rouge is still too

rough, and it may be useful to continue the polishing with precipitated sulphate of lime.

§ 8. **Polish Attack.**—This consists of adding to the polishing material some liquid, which would be inert by itself, but which exerts a slight chemical action when assisted by the friction of the rubbing. In this way ammonia water not only does not oxidise steel but preserves it from oxidation, yet, when soft steel is rubbed on the polishing block and a little ammonia water is added, the surface becomes iridescent, and the hard constituents are readily distinguished from the softer ones. Another liquid successfully adopted by M. Osmond is infusion of liquorice-root, made by steeping the root in cold water for a few hours and filtering off the clear liquid. It quickly spoils, and should not be kept for more than eight days. After polish attack it is best to rub the metal with rouge to decolourise it and efface the bas-reliefs.

§ 9. **Attack Proper.**—For carburetted irons Osmond does not consider that hydrochloric acid, sulphuric acid, citric acid, or chromic acid presents any advantages over the dilute nitric acid generally used. The halogens which attack iron, separating the whole of the carbon, have a simpler action than the acids, and therefore tincture of iodine has been found quite satisfactory. This tincture should not be made with absolute alcohol, as the action is very slow and irregular. That of the pharmacopœia is suitable. The section to be attacked is touched with a few drops of the liquid and left till the colouration is satisfactory. The section is then washed with alcohol, and dried by wiping with fine linen.

§ 10. **Mr. Stead's Method.**—This is practically the same as that of M. Osmond. The rough grinding is done on glass plates, on which emery paper is gummed. Instead of using crocus rouge for the preliminary polish-

FIG. 1. The Whirling Table.

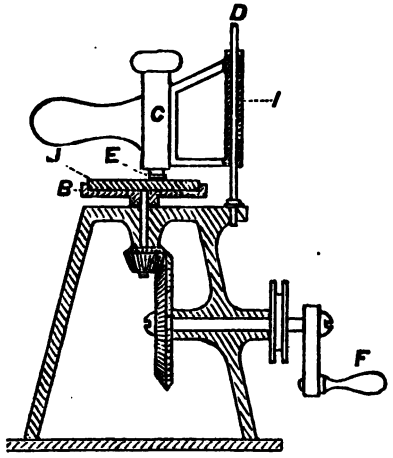


FIG. 2. The Stead Machine.

ing, he finds the diamantine powder used by jewellers for polishing steel much more rapid in its action. The cloth, chamois leather, and parchment are stretched on conical blocks, such as those which Professor Arnold uses, only they are smaller, and are kept in position by means of metal rings, the advantage being that they may be fitted into a revolving polishing machine. The system of rubbing the finest rouge into parchment, and washing off all that will not penetrate into the pores of the material, is very excellent; it gives a surface which never produces any scratches, and polishes perfectly. For general work the final polishing is done on dry chamois leather with the finest rouge, but much finer work is accomplished by polishing on wet parchment.

The examples in this book have been partly done by hand on emery and rouge pads and partly by means of a revolving polishing machine, using a rouge lap for finishing. The latter is preferable where available, but good sections may be prepared by hand by using different grades of emery paper glued on to wood blocks, and rouge on wash leather for finishing.

§ 11. **Mechanical Motors.**—1. *The Whirling Table* (fig. 1) consists of a metal platform, on which a bob covered with cloth is fixed. On this cloth water and a little rouge are used. The handle is turned by the right hand, and the section to be polished held in the left hand. It can be fixed vertically or horizontally.

2. *The Stead Machine*[1] (fig. 2). It contains a circular table *B*, upon which the various grinding discs are placed, and which can be rotated by means of the handle *F*. The specimen holder *C* consists of a cylinder of brass, the lower extremity of which is closed, and has a projection of about five-eighths of an inch in diameter, upon which the crown or cap *E* is placed. The specimens are cemented to the crown, several of which

[1] *Jour. Iron and Steel Inst.*, p. 305, 1894.

accompany each machine. By means of the frame *I*, and the fixed vertical shaft or pinion *D*, the holder can be moved completely round and away from the table *B*; but when the specimens are being ground, it is only moved so that the whole of the grinding surfaces are traversed, namely, from the centre to the outside of the discs. The grinding is done dry, and as a consequence the specimens are liable to get hot, and in order to cool the crowns the holder *C* is filled with water and a plug fitted at the top to prevent its escape.

The grinding discs consist of: (1) A coarse emery wheel. (2) A fine flour emery wheel. (3) A plate-glass disc, upon which is glued fine emery paper, or the plate itself may be coated for a foundation with a thin wash of gelatine and chrome alum, and, after drying, be washed with a thin layer of glue, upon which washed emery powder is dusted; when dry, this forms an excellent grinding surface. (4) A glass plate, upon which is glued a piece of the finest emery paper, or the glass itself may be coated with the finest washed emery powder, as above. (5) A slightly conical block, upon which is stretched and kept in position by means of a metal ring a sheet of smooth cloth. The cloth is laid on the surface of the block and the ring forced down into position. Upon this block crocus powder is used. (6) This block is similar to the last, but, instead of cloth, fine wash leather is used. On this is placed the very finest gold rouge.

The rough-sawn sections are soldered to the crowns with a very fusible solder, or with pure tin. The crowns are held over a spirit lamp and a little chloride of zinc solution dropped on the surface, and this is followed by a little powdered solder, which soon melts. The section is cleaned, moistened with the zinc solution, and dropped on to the molten solder, which is then allowed to set.

The crown is now slipped on to the holder and the coarse emery wheel used to grind the section flat. As

NOT FOR LOAN

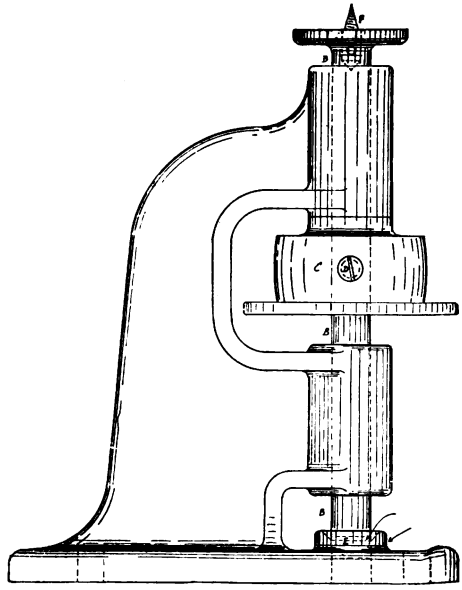

FIG. 3. The Hawkins Machine. Page 23.

FIG. 4. Photo-Micrographic Apparatus. Page 29.

soon as this is accomplished the fine emery wheel is introduced and the grinding continued until the scratches from No. 1 wheel are obliterated. By turning the crown at right angles after every grinding, the examination for scratches is very simple, as they will be seen to be at right angles to the marks produced by the grinding surface following. The other discs follow in order until the sample is perfectly smooth. Mr. Stead states that he finds it an advantage to etch the specimen with the crown attached, for, if the etching should be carried too far, it is easy to slip it on to the machine and re-polish it. This is not advisable when a long and deep etching is desirable, as the crown itself is partially dissolved and the copper from the brass is precipitated on the polished surface.

When it is desired to remove the specimen the crown is heated, the specimen being held by a pair of forceps. The moment the solder softens the crown drops off, leaving the sample ready for etching and examination.

3. *The Hawkins Machine.* This is an arrangement devised for students' use in the author's laboratory by his colleague, Mr. W. Hawkins, and made by Mr. C. Taylor, of Bartholomew Street, Birmingham. It is represented in fig. 3. The machine consists of a cast-iron bracket, through which a wrought-iron spindle works. At the centre of the bracket a three-inch pulley, with a rim on the lower side, is kept in position on the spindle by means of a screw. This pulley affords a means of keeping the spindle in position at the top portion of the bracket, and thus avoids the use of a collar or lock-nuts. At the end of the spindle, at the base of the bracket, and fitted in the same, is a gun-metal step-bearing to steady the spindle; this can be replaced at any time when worn out. At the top portion of spindle is a left-hand screw, on which the polishing lap is fixed, being screwed down to the collar.

These brackets are placed six in a row, and all driven from one countershaft at the back of the bench. The top of the bench just allows the screw and collar, as shown at *F*, to stand clear of the woodwork. In order to prevent dirt getting to the spindle a felt pad is placed round the spindle at *B*, underneath the collar. The whole of the driving belt is concealed beneath the bench, and a trap door, fixed in front of the bench, is provided for access to the working parts when necessary.

On the countershaft are placed six driving pulleys, twelve inches diameter, which drive the six spindles by means of the pulleys *C*, using a leather belt, half crossed. The power is supplied by an electric motor, and the speed of the spindle is about 2000 revolutions per minute.

The bobs or laps are made of wood, flat on one side and with rounded edge on the under side. The flat side is covered either with buff or wash leather, and can be obtained from three inches to nine inches diameter.

§ 12. **Heat Tinting.**—Etching polished metals with corrosive liquids is more or less liable to lead to the confusing of the constitutional and crystalline structures. With feeble etching, as a rule, the constituents are rendered visible ; with strong etching the granular, and often the crystalline, structures are developed. By heating polished sections of iron at different temperatures the constituents become differently coloured by oxidation films, and may therefore be detected. Mr. Stead terms this the constitutional method, and has the advantage over etching, that none of the metal is dissolved and the surface remains flat.

Some alloys contain a fusible constituent, which melts and exudes from the surface before any oxidation can occur, in which case oxidation is not available. Different tints can, however, be obtained by gently heating the section in an atmosphere containing slight traces of

iodine, bromine, or sulphuretted hydrogen. In such cases the specimen may be heated in a box, fitted with a glass lid, and air, which has passed over iodine, bromine, or sulphuretted hydrogen, may be forced over the hot metal. The polished section may contain moisture in the pores, so that it is advisable to heat it to about 120° C., and slightly re-polish while hot before making the observation. When the desired tints have been developed the section should be rapidly cooled so as to avoid any further change. For this purpose a bath of mercury is useful.[1]

[1] *Jour. Iron and Steel Inst.*, page 140, No. 2, 1900.

# CHAPTER III.

## THE MICROSCOPE.

§ 13. In the first place it should be understood that a very simple pattern microscope is all that is necessary for the examination of micro-sections of metals, the only essentials are :—that the instrument should have a firm and fairly heavy stand ; that the objectives should give a flat field ; that they should be achromatic and possess clear definition. A mechanical stage is quite unnecessary, neither is a polarising arrangement required. It is convenient in special cases to have the eyepiece of lowest power fitted with crossed cobwebs for centring and goniometric measurements, and to have attached a camera lucida for drawing objects. A bull's-eye condenser, or silver side-reflector, is also necessary for condensing light on to the object or on to the vertical illuminator.

If the operator wishes to limit the cost to the lowest figure he need not obtain more than three objectives. The ones most used by the author are 2 inch, 1 inch, and $\frac{1}{4}$ inch, which give magnifications from 30 to 220 diameters, and if a high-power eyepiece is used he may get amplifications from 100 up to 600. In addition to these a vertical illuminator is necessary. A very good and cheap one is supplied by Ziess.

Two kinds of illumination are used in viewing the structure of a metal, termed respectively oblique and vertical illumination. In the former the microscope is generally tilted at an angle and the light condensed on the object, which then reflects the light up the axis of the tube. In many cases this gives but little information. For vertical illumination a piece of glass or other transparent reflector is arranged at an angle of 45 degrees so as to reflect a horizontal beam of light at right angles on to the object, which then reflects the light vertically up the tube of the microscope to the eye. This glass is arranged in a brass fitting, which is screwed on to the stem of the microscope above the objective; in fact, the apparatus is so devised that it simply forms an extension of the tube, and the objectives are then screwed into it in the usual way. This reflector can be completely rotated in a vertical plane so that it may easily be thrown in or out at pleasure. When it is quite vertical it does not interfere with the vision for oblique light. One thing, however, is essential, namely, that when the reflector is placed at an angle of 45 degrees for direct illumination the tube of the microscope must be exactly at right angles to the incident beam of light, especially when high powers are being used. Instead of the reflector being arranged at the bottom it may with equal propriety be placed at the top, just below the eyepiece.

A still better arrangement, especially for photographing the sections, is to replace the plane glass reflector by a right-angled prism, placed in a similar brass mounting, and capable of similar rotation. This is based on the well-known principle that when a beam of light strikes a plane at a greater angle than the limiting angle it is totally reflected. In cases where an objective of not less than 1 inch is used a simple piece of thin glass or clear mica may be placed above the object and between it and the objective, which gives practically the same result.

As far as possible work should be carried on by daylight, and when this is impossible an oil lamp is a very convenient source of light. During daylight, sunlight reflected from white clouds, or by a wall of the same colour, should be preferred, as direct sunlight is not advisable. The light may fall direct on to the reflector or it may be condensed by means of a condenser.

§ 14. **Photo-Micrography.**—This is simply the art of photographing a magnified image of an object placed on the stage of a microscope. The image, instead of being received in the eye, is projected on to the ground-glass screen and properly focussed. When this has been satisfactorily done, the screen is replaced by the sensitised plate and the image photographed thereon. Various sources of illumination have been used from time to time, from the sun to the oil lamp, the latter requiring a long exposure with high powers, but it may be usefully employed for very low power work. A single wick used edgeways is most suitable. Incandescent gas is very good for plain work, but is unsuitable for high powers where critical light is used, *i.e.* where the image of the illuminant is focussed sharply on the specimen. It is desirable that the source of light should approximate as near as possible to a point of light, which is practically obtained in the electric arc. Certainly this point is always shifting, but with a good mechanical arrangement and proper attention this may be overcome, as seen by the illustrations in the present work, most of which have been taken by means of an electric-arc illuminant. An incandescent electric lamp of 60 to 110 volts pushed a little beyond its stated voltage, say to 65 and 115 respectively, has been found to yield excellent results, requiring only an exposure of about one minute. By this forcing of the lamp its life is considerably diminished, but the light emitted is beautifully photogenic. Limelight is largely used, being more

readily available. A detailed account of the best kind of limelight jet, with precautions and instructions for use, will be found in Spitta's *Photo-Micrography*, published at the Scientific Press, London.

In photographing metal sections, which are necessarily opaque, direct illumination is, in the majority of cases, essential, and the beam of light from the illuminant must be at right angles to the axis of the microscope. The camera may therefore be used in a horizontal or in a vertical position. If the source of light is upright, in the usual vertical position, then the camera must be vertical, with the glass screen at the top and the lens at the bottom. The microscope will also be placed vertically beneath and projecting into the camera extension. This arrangement is the one adopted by the author, and shown in fig. 4. It consists of a wooden stand with a vertical slot and screwed brass plates at the back side, into which the screws of the camera base are screwed so as to support the apparatus. It was found that this did not make it perfectly rigid and strictly vertical, so that a cord was attached to the top of the camera and passed over a pulley at the top of the stand. The other end of the cord was attached to a lead weight which hung down behind. By this means perfect steadiness was obtained. If the camera is used in the horizontal position, then the beam of light from the illuminant must fall perpendicularly on to the reflecting mirror or prism inside the microscope.

To perfectly illuminate opaque objects for photographing it is generally necessary to remove the cover glass, if one has been affixed, for the reflections caused by it are detrimental to the production of a good negative. A condenser is used to focus the light from the illuminant on to the vertical reflector, or on to the object when oblique light is employed.

The production of a photograph involves, as is very well known, two operations, the production of the

negative and of the paper print. The negative is produced in the following way: The section is placed under the microscope, the upper end of which is inserted into the camera, which is arranged to slide vertically, the lens of the camera having been first removed, as the microscope itself performs this function. In fact, all that is required is a simple box, with focussing screen and dark slide. The junction between the camera and microscope is made light-tight by means of a sleeve of black cloth tied round the camera bellows and also round the stem of the microscope. The object is then carefully focussed on to the dark slide by means of the focussing screw of the microscope. The image may be increased or diminished in size by raising or lowering the camera. The eyepiece of the microscope may or may not be used, but if it is not used the interior of the tube must be blackened so as to prevent reflection of light.

As before mentioned, direct light is obtained by means of a right-angled prism, fixed in a suitable fitting, which can be screwed on to the microscope between the stem and the objective. When properly adjusted and focussed the dark slide is placed in position and the source of light cut off by placing some opaque object in front, such as wood or cardboard, while the shutter is being drawn out. The light is then allowed to fall on the illuminator until sufficient exposure has been made, when it is again cut off and the shutter pushed in. The dark slide is now removed and the image viewed again on the focussing screen to see that it has not moved. The time of exposure will be governed by the nature of the light and by the amount of light reflected by the section. With an ordinary section and using an arc light, ten seconds are enough; with dull sections about fifteen seconds are required. With a very bright section we have found ten seconds to produce over-exposure.

Development is either effected by placing the plate

in the developer, which is previously poured into the developing dish, or by pouring the developing mixture over the plate in a developing dish, film upwards. The developer is kept constantly moving over the surface of the exposed film. When the image appears with every detail, and has acquired sufficient density (which can be tested by looking through the plate held up to the light), it is then carefully washed under a water tap, and afterwards placed in the fixing bath. The plate is fixed when no white part is seen on its under-surface. It is then washed afresh. When sufficiently washed (about two hours being required) it is removed from the water, placed upright to allow the water to drain off, and allowed to dry of its own accord, as extra heat may dissolve the gelatine.

The plates used for the photographs of this work are the Ilford ordinary dry plates, and the developing formula is that given upon the boxes, viz.:

| | |
|---|---|
| Stock solution B, water - - - - | 5½ ounces. |
| Metabisulphide of potassium, - - | 70 grains. |
| Pyrogallic acid, - - - - - - | 1 ounce. |

For working, take 1 to 2 ozs. of stock sol. B and water to make up to 20 ozs. Mark this sol. No. 1, and for No. 2 use

| | |
|---|---|
| Carbonate of soda crystals, - | 2 ozs. (avoirdupois). |
| Sulphate of soda, - - - | 2 ozs. |
| Potassium bromide, - - | 20 grains. |
| Water to make up to - - | 20 ozs. |

Use equal quantities of No. 1 and No. 2.

After developing, rinse plate in water before placing in fixing bath, which is made up of sodium thiosulphate, 1 lb. in 40 ozs. of water. Allow to remain in this solution several minutes after fixing is apparently complete. Wash in running water for one hour, and dry in room free from dust.

To print, well clean the back of the negative and place it in printing frame with film inside; stop off unnecessary parts with mask of black paper, and lay the sensitised

paper on the film of the negative, insert the back and clamp up tightly. The length of exposure must be judged by the density of the negative, the brightness of the light, and the distance from the light. Daylight is too rapid. The print is developed, fixed, and washed in the same manner as the negative, but the developing solution may be diluted with a little water. Prints must be completely fixed before washing, and then thoroughly washed, or else stains will appear. When sufficiently washed they should be pressed between flat surfaces of clean linen to remove excess of water, and dried gradually. The paper used is bromide paper, Morgan & Kidd's white enamel being as good as any.

# CHAPTER IV.

## STRUCTURE OF IRON.

§ 15. The structure of iron may be studied by microscopic examination of polished and etched sections, and by its fractures. The first method reveals the natural condition of the metal and the latter the planes of weakness induced by stress. By the aid of different solutions we find the various constituents are acted upon differently, so that some of the components are dissolved, leaving a skeleton having the structure of the original.

It has already been indicated that impure metals and alloys bear a close resemblance to complex crystalline rocks, which are made up of distinct crystalline minerals. Their nature, size, shape, and orientation, and through these the structure and physical properties of the metal as a whole, seem to depend chiefly on the chemical composition, the mechanical treatment, and the mode of heating and cooling. By these means new combinations may be formed, and one set of minerals gives place to another. In accordance with a suggestion made by Mr. Howe, mineralogical names have been given to the various constituents of iron and steel in order to facilitate their identification.

§ 16. **Ferrite** is the free iron of Sorby. It consists of nearly pure iron, and is the chief constituent of wrought-

iron and mild steel, in which it exists as polyhedral grains of very irregular form. In general, it decreases as the amount of combined carbon increases, and is practically absent from hard steels, white cast-iron, and ordinary pig-iron. Howe considers the crystals to be interfering cubes or octahedra. It is also an integral constituent of pearlite, of which it forms about two-thirds the bulk. In very grey pig-iron it is probably present in small quantity, forming a network round the crystals of the other components. These crystals of carbonless iron are left white and brilliant when treated with a solution of iodine. Strong nitric acid also does not stain them. Ferrite may contain other elements, which form isomorphous mixtures with iron. It is the softest constituent of iron and steel.

§ 17. **Cementite.**—Carbon of Normal Carbidė (Ledebur), Reheated Carbon (Osmond and Werth), Carbon of Cementation (Caron). This is the intensely hard compound of Sorby. It was first clearly discovered in steel made by the cementation process. It is hard and stands in relief when soft steel is polished, but is practically absent from the hardened steel. Dr. Müller and Sir Frederick Abel independently isolated it, and found it to contain 93·33 per cent. of iron and 6·67 per cent. of carbon, which corresponds to the formula, $Fe_3C$. It is soluble in boiling strong sulphuric acid, and also in boiling concentrated hydrochloric acid. It remains bright after a polished section is treated with iodine solution. Being very hard it stands out in relief when the steel is polished with the finest rouge on parchment laid on a soft support, such as wood. A similar compound carbide is found in manganese steel which has been submitted to cementation. Cementite will scratch glass and felspar, but not quartz; it therefore has a hardness of about 6·5. Free cementite does not occur in normal mild steel. It is an essential constituent of pearlite.

§ 18. **Pearlite.**—This is the pearly constituent of Sorby, and is made up of an intimate mixture of ferrite and cementite. It is found in steel which has been slowly cooled from a high temperature, and may be lamellar or granular in structure. Howe suggests that it does not contain more than 0·67 per cent. of carbon, but when steel contains 0·9 per cent. of carbon the whole mass appears to be composed of pearlite. It consists of alternating plates of ferrite and cementite, or cementite and sorbite, or grains of cementite embedded in ferrite or sorbite. Baron Jüpter considers that the cementite of the pearlite consists chiefly of a carbide having the formula $Fe_{12}C_4$, but that the sorbite perhaps contains $Fe_9C_3$. It appears that cementite and ferrite or sorbite usually unite in certain proportions, as far as possible, to form pearlite, so that any excess of cementite or ferrite remains free. Thus pearlite may be accompanied by either free cementite or by ferrite, but not usually by both together in the same region. Hence, as the proportion of combined carbon increases in unhardened metal from nil, we have first ferrite, then ferrite with a portion of pearlite, which increases up to 100 per cent. at 0·89 per cent. carbon, and then diminishes as the proportion of combined carbon increases, being replaced more and more with free cementite. Thus high carbon steel, say 1·5 per cent. carbon, contains little pearlite and much cementite. Sorby considers that white cast-iron consists of about two-thirds pearlite and one-third cementite; while Spiegel-eisen contains about equal quantities of each. If steel is long exposed to a high temperature, the pearlite draws together and separates itself in more perfect crystals from the ferrite or cementite which accompanies it. If, however, the pearlite be initially associated with graphite, its cementite apparently tends to split up into graphite and ferrite at a moderately high temperature. Pearlite may be coloured dark by iodine solution, and its presence is

best revealed when the steel is polished in relief and treated with a filtered infusion of liquorice-root in cold water. The laminae of pearlite are alternately hard and soft, the cementite being hard and the ferrite soft. Fig. 5 is a photograph of pearlite kindly supplied by Mr. J. E. Stead.

§ 19. **Sorbite.**—This is a transition form passing into pearlite, intermediate between troostite and pearlite; probably having the composition $Fe_9C_3$, and existing in a solution of iron. It may be simply unsegregated pearlite. Sorbite is obtained by a moderately slow cooling, as in the cooling of small samples in air. Also by quenching with water at the end of the recalescence period; or by quenching in lead. It is tinted brown by etching in dilute acids or in iodine solution. It is also coloured by solution of liquorice root.

§ 20. **Troostite.**—This is a transition form between martensite and pearlite, so that when a hardened steel has been partially annealed the martensite is only partially changed to pearlite, and then contains some troostite. According to Osmond, it is contained in steels of various carbon contents on quenching at certain temperatures. It is revealed by polishing the steel on parchment, moistened with a solution of liquorice-root or nitrate of ammonia, which turns it brown. It is softer and more readily acted upon by acids than martensite. By etching with an alcoholic solution of hydrochloric acid (1 part hydrochloric acid in 100 parts of alcohol), martensite remains unaltered, while troostite is coloured dark. It is probably a solution of the carbide, $Fe_9C_3$, in iron.

§ 21. **Martensite** —This is the very hard substance of which hardened steel consists. It imparts a characteristic structure to polished and etched surfaces of hardened steel. The appearance is that of interlacing rectilinear

FIG. 5. Pearlite. ×550 dia.

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FIG. 6. Austenite and Martensite. ×550 dia.

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fibres roughly arranged in triangular shape, which may be coloured by tincture of iodine. It is probable that ferrite and cementite unite to form martensite when the steel is highly heated, and by rapid quenching the structure is retained. Arnold suggests that the term should be used for hardened steel containing the same amount of carbon as pearlite. Osmond considers that martensite corresponds to the maximum amount of allotropic iron and of hardening carbon that may be retained, by sudden cooling, in carburised irons in which the carbon content of the mixed crystals does not exceed 1·1 per cent. before quenching. It is most readily obtained by rapid quenching of small samples. It is very coarse in steel with 0·5 per cent. of carbon, and very fine in steel with 1 per cent. carbon.

§ 22. **Graphite** is a principal constituent of grey pig iron, and easily recognised by its colour and peculiar property of forming curved lines.

*Temper Graphite* is probably graphite which has separated from steel by prolonged heating at a high temperature and slow cooling. It assumes small irregular rounded masses.

§ 23. **Austenite.**—This term is applied by Osmond to a mineral in high carbon steels which is developed by very sudden quenching from a high temperature. It is softer and less magnetic than martensite, with which it is generally associated. The structure is developed by polishing on parchment, moistened with liquorice solution or with nitrate of ammonia. The austenite remains white, the martensite becomes brown, and often appears in a zigzag form. The relative hardness is tested by scratching with a sewing needle. On account of its low degree of hardness, and because it is only stable at very high temperatures, Baron Jüpter considers it a solution of elementary carbon in iron. Fig. 6 shews a sample of austenite kindly supplied by Mr. Stead.

# CHAPTER V.

## CAST IRON AND PIG IRON.

§ 24. Pig iron consists of iron with upwards of 1·8 per cent. of carbon and various other elements in greater or less proportion, of which silicon is always present, and generally sulphur, phosphorus, and manganese. Constituents other than the above may be considered as impurities, unless such elements are purposely introduced so as to produce brands of iron for specific purposes. In this way we may get chromium, tungsten, molybdenum, aluminium, etc., as chief constituents of the pig iron, or alloys of these metals with iron and carbon may be made in crucibles or furnaces. In ordinary pig iron the proportion of elements other than iron is about seven per cent., but sometimes very much more. Pig iron, which is cast in open sand moulds when a blast furnace is tapped, is D-shaped in section, about three or four inches square, and about three feet long. It is arranged into a variety of classes, according to the colour, texture, size of the crystalline plates, and general character of the fractured surface. When the pig iron is obtained entirely from ore it is termed "All-mine" iron, which is graded from Nos. 1 to 8, or more commonly from No. 1 to 4 for foundry purposes, and No. 4, mottled and white. In the southern parts of the United

States nine numbers are used, viz., Nos. 1 to 3, foundry; 4 and 5 are termed Nos. 1 and 2 soft; No 6, silver grey; No. 7, grey forge; No. 8, mottled; and No. 9, white pig iron. Nos. 4, 5, and 6 are silicious irons, containing 4 to 6 per cent. of silicon. In this country, that containing the largest grains and largest crystals of graphite is No. 1, and this is found to be richest in silicon.

As a general rule, in passing through the series from No. 1 to white iron, the combined carbon and the sulphur regularly increase, while the silicon steadily diminishes, when the samples are prepared under practically the same conditions. Although there is but little difference between pig iron and cast iron, the latter term is used to express the metal obtained by remelting pig iron and casting it into various moulds, while pig iron is simply a variety of cast iron, cast in a particular form. Cast iron when in the liquid state may be considered as a saturated solution of carbon in iron, which generally contains about three per cent., depending upon the nature and amount of other elements present. Chromium and manganese increase the solvent power for carbon, and silicon acts just in the opposite direction. Iron with 20 per cent. of silicon only dissolves about one per cent. of carbon. It is, however, unusual to meet with less than 2 per cent. or more than 4·5 per cent. of carbon in cast iron. Up till recently the condition of carbon in cast iron has been considered as existing in two forms, viz., as combined carbon in white iron and as free carbon in grey iron. One thing is beyond question, that carbon does separate from iron in the form of crystalline graphite and makes the iron grey in colour, but whether carbon does unite chemically with iron in the white variety, or exists as a solution in the iron, is not yet satisfactorily determined. It is probable, however, that a definite compound does exist, similar to, if not identical

with, the free carbide, $Fe_3C$, in steel. Possibly there may be more than one compound, or more than one alloy, dissolved in the main mass of iron.

When cast iron is in the fluid condition its composition is probably uniform, except in the case of very grey pig iron, when graphite separates out in beautiful plates, termed "kish"; but on cooling, according to the rate at which it solidifies, the carbon will separate, or remain in close union with the iron. When both conditions prevail, the iron has a mottled appearance, due to the carbon being partly in what is termed the combined form, and partly in the free form. Slow cooling tends to the formation of grey iron, and quick cooling to that of white or chilled iron. The production of white or grey iron respectively is not only due to rate of cooling but also to the presence of elements other than carbon, some of which increase the solubility of carbon in iron and others act in a totally opposite direction; hence, irons which are very white or very grey are not materially changed by rate of cooling, and mottled iron may be produced by the counteracting influences of oppositely tending elements.

The different kinds of pig iron act differently when treated with acids. On dissolving white cast iron in hydrochloric acid, the carbon combines with hydrogen to form ill-smelling hydro-carbons, which are volatile. With nitric acid, white iron and the contained carbon are dissolved, imparting to the solution a characteristic brown colour. On the other hand, with grey iron, the carbon, being in the free form, is insoluble in the above acids, and is left behind as a black residue.

All cast iron contains silicon in quantities varying from 0·1 to 4 per cent., and in case of special "silicon pig iron" from 10 to 18 per cent. It is the chief factor in determining the condition of the carbon, causing the separation of carbon as graphite, and may be said to be an essential constituent of grey cast iron. White cast

iron is hard and brittle, but on the addition of sufficient silicon it becomes grey, soft, and strong. With excess of silicon it again gets hard and weak. A little silicon promotes soundness in castings and eliminates blow-holes, it therefore increases the density and raises the crushing strength. White iron shrinks more than grey iron during solidification, and as the hardest irons shrink the most, this property depends on the proportion of combined carbon, and may be reduced by adding silicon. The condition of silicon in cast iron may be similar to that of carbon, existing in the combined and the free state, although the latter may be a silicide of carbon, or even silicide of iron, corresponding to cement carbon, $Fe_3C$. Aluminium in cast iron acts in a similar way to that of silicon by liberating free carbon, diminishing the shrinkage, and increasing the strength.

Sulphur in cast iron causes the carbon to assume the combined state, thus making the metal harder, weaker, and more brittle. Grey iron, rich in sulphur, frequently contains unsightly black patches, and with much sulphur in the presence of high silicon, two distinct alloys separate from each other, the more silicious one being at the bottom and the more sulphury one at the top. With small amounts of sulphur the distribution is unequally disposed through the mass. In some classes of hematite pig iron the sulphur seems chiefly to segregate in the middle portion.

Phosphorus exists in pig iron probably as a phosphide, and produces a very fluid metal, adapted to the production of fine castings, but such metal is weak and brittle when the amount of phosphorus exceeds 1 to 1·5 per cent. Ordinary strong castings may contain as much as 0·5 per cent. Phosphorus probably hardens cast iron, but does not appear to have any effect on the condition of the carbon.

Manganese in quantities less than 1 per cent. does not materially affect the properties of cast iron, but 1·5

per cent. makes the iron appreciably harder. When only a small quantity of silicon is present and 2 per cent. and upwards of manganese, the iron is white with large brilliant crystalline plates, very hard and brittle, and termed "spiegel-eisen." When the amount of manganese exceeds 20 per cent. the grain becomes closer and the alloy very brittle; it is then termed "ferro-manganese." An alloy of iron and carbon containing, say 20 per cent. manganese and 10 per cent. silicon, is produced and termed "silicon-spiegel." The general effect of manganese in cast iron is to make it white, hard, brittle, and to increase the shrinkage during solidification.

Chromium is only present in very small quantities in ordinary cast iron, and its influence is negligible. Rich alloys are, however, specially prepared, termed "ferro-chromes." They are somewhat refractory, very fluid when perfectly melted, and very rapidly solidify. Rich ferro-chromes are capable of dissolving large quantities of carbon, according to the amount of chromium present. Chromium therefore makes cast iron white, hard, and brittle. It does not tend to produce soundness in castings nor to eliminate sulphur. The fracture of rich ferro-chromes is very characteristic, showing a marked acicular (needle-shaped) structure. Behrens has shown that ferro-chromes, when etched with an acid, yield non-magnetic, bayonet-shaped crystals, which have a hardness of 7·5 and consist of chromium ferro-carbide. The hardness therefore increases with the amount of carbon.

Titanium is only present in pig iron in small quantities, the oxide being very difficult to reduce. It appears to act somewhat like silicon, being found in the largest proportions in grey irons. A compound of titanium is found in the "bears" of some blast furnaces, known as "cyano-nitride of titanium." It consists of small crystals of the cubic system, having a metallic

lustre and bright red colour. Pig iron containing titanium presents a peculiar black mottled fracture, probably due to the separation of a titanium carbide. Hogg[1] has observed similar crystals in rich ferro-manganese. For fuller information concerning properties of cast iron, see Turner's *Metallurgy of Iron*, published by Griffin & Co.

§ 25. **Malleable Cast-Iron.**—When cast-iron articles of small section are embedded in powdered hematite, or other suitable iron ore, packed in iron cases and heated to a cherry-red heat for a few days, they become very malleable and are said to be annealed. There are two classes of malleable castings in general use.

1st. The older class is produced from white pig-iron of good quality, preferably that from Cumberland hematite ore. The castings after cleaning are packed in wrought-iron boxes, and completely covered with particles of hematite about $\frac{1}{8}$ inch in diameter. The cases are then placed in the furnace, gradually raised to a red heat and maintained at that temperature three or more days, according to the degree of softness desired and the character of the castings.

2nd. "Black heart" castings. These are American malleable castings which retain the original carbon practically unaltered in amount in the central portion, but the carbon is changed from the combined to the graphitic form. The outside portions however contain less carbon than the interior. If a piece of malleable cast iron is strongly heated and quenched in water it becomes intensely hard, showing that the mass of the carbon is not removed by the annealing process but only modified.

Mr. J. Stead[2] has investigated the nature of malleable castings by operating with cast round bars. He found

[1] *Brit. Assoc. Report.*, 1893, p. 721.
[2] *Cleveland Inst. of Engineers*, Dec. 16th, 1895.

a transverse section taken from one end, $\frac{5}{8}$ in diameter, to consist of five different concentric zones. The outer one had a thickness of 0·072 inch, and consisted of iron and silica, the latter appearing to have been deposited in the joints of the iron crystals. The second zone consisted of iron free from carbon, but the iron was crystallised in a columnar form, radiating from the exterior surface towards the centre. The third zone is a mixture of iron and pearlite. The fourth zone appeared to be all pearlite. The fifth zone had the appearance of steel with 1·4 per cent. of combined carbon, and consisted of large meshes of cementite, with intervening pearlite and a considerable quantity of graphite. See Fig. 7.

It appears probable that, when white cast-iron is annealed, the combined carbon in the form of pearlite is set free as graphite. If the alteration were confined to the surface it might be assumed that the carbon was burned off; but the change goes right to the centre, and as much of the carbon is retained it proves that a soft and tough casting may be obtained by simply changing the hardening carbon to graphite or temper carbon. When this change has been completely effected no advantage is gained by heating with fresh hematite, and the outer layer does not materially increase in thickness nor the central portion become more or less crystalline.

§ 26. Mr. Howe[1] considers that composition governs the properties of cast-iron in the same general way as in the case of steel. When the carbon is wholly in the combined form, as in white cast-iron, there is a continuous chain from the mildest steel to the whitest cast-iron. Grey cast-iron may be regarded as graphite associated with steel or with cast-iron, according as the percentage of combined carbon is low or high. In the

[1] *Trans. Amer. Inst. of Min. Eng.*, 1901.

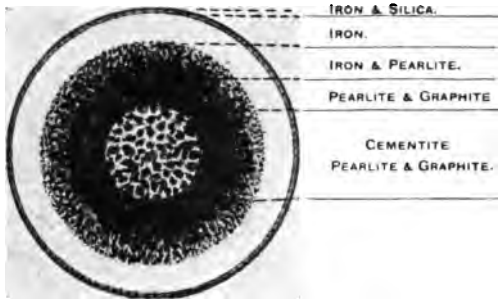


FIG. 7. Malleable casting.

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FIG. 8. Grey pig iron, transverse section.
×50 dia.

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graphiteless series the general trend of the curves of ductility, hardness, and tenacity may roughly be plotted. In the graphitic series, when the graphite is constant, the variation in the combined carbon in the matrix should produce similar results to those of the graphiteless series—that is, the hardness should increase and the ductility diminish with the combined carbon, and the tenacity as a whole should attain a maximum at about 1 per cent. of carbon. With constant combined carbon the strength, ductility, and hardness should decrease as the graphite increases. Increase of combined carbon substitutes cementite for ferrite, and so increases hardness and diminishes ductility.

With regard to the effect on tenacity two explanations are possible, depending on the strengthening action of the hard cementite, or on the hard allotropic modification of iron surrounded by a softer and more ductile ferrite. In the lower carbides the harder part is discontinuous, and accommodates itself to the flow of the ferrite; but when the carbide increases, the cementite, or whatever it may be, forms a more or less continuous skeleton, which does not yield, but tends to imitate local fractures, and as these spread they produce weakness in the whole mass. The strongest steel contains about 1 per cent. of carbon, but in cast-iron there is graphite to be considered, and for greatest strength the combined carbon should be greatly in excess of the graphite.

Carnot and Goutal[1] consider there are four kinds of carbon in pig-iron and steel—graphite, graphite temper carbon, carbide carbon, and hardening carbon. The two former are free, the third in combination with the iron, and the last in solid solution, or in the form of combinations dissolved in the iron, but decomposable by cold dilute acids, while the carbide carbon is not decomposed. In addition to carbon, the authors investi-

[1] *Annales des Mines*, vol. 18, pp. 263-300.

gated the condition of manganese, sulphur, phosphorus, silicon, and arsenic in cast-iron. They conclude that: (1) Sulphur is usually combined nearly entirely with manganese as manganese sulphide, MnS, the excess, if any, being present as ferrous sulphide, FeS; (2) phosphorus is combined directly with iron as iron phosphide, $Fe_3P$; (3) arsenic is almost always free, or exists as a solid solution, but after hardening it is partially combined with iron as iron arsenide, $Fe_2As$; (4) silicon is usually in the free state. It can also unite with iron and manganese to form manganese silicide, MnSi, and iron silicide, FeSi, but the latter is dissociated on slow cooling, or at least cannot then be isolated. The silicide, MnSi, is not dissociated by cooling. Ferro-silicons contain both FeSi and $Fe_3Si$. Silicon-spiegeleisen contains a double silicide, $(MM^1)_3Si$; (5) carbon is combined with both iron and manganese, forming double carbides, $Fe_3C$ and $Mn_3C$.

§ 27. The internal structure, as seen in microscopic sections, not only differs enormously in the three different varieties of cast-iron, but in the case of grey iron the complex character varies considerably in the different grades. In No. 1 pig-iron, or very grey iron, the most striking feature is the broad plates of graphite scattered indiscriminately in all directions and forming a considerable proportion of the whole bulk. "The structure of the surrounding metal is much more complex than might have been expected, and cannot be understood unless a power of 400 linear is used. In the first place we see what I take to be iron free from combined carbon, usually, but not invariably, occurring as a moderately stout layer over the graphite. Then over this is the pearly compound seen in cast steel, probably in a condition somewhat degraded by the setting free of graphite. Lastly, as far away from the graphite plates as is possible, occurs a relatively small quantity of a

metallic substance, often full of included foreign matter similar to the hard compound seen so well in white cast-iron, in a condition greatly modified by the presence of impurities thrown off as a final residue. It seems almost certain that, in the first place, graphite crystallised out, leaving alongside it iron free from carbon. Then the pearly constituent solidified, and in doing so threw off an impure residue."[1]

In some grey pig-irons little or none of the layer of iron free from carbon is present, but much more of the above-mentioned residual matter. Also the graphite, instead of being distributed confusedly through the mass, is collected into irregular radiating groups, and while, on the whole, it has crystallised out first, some of the pearly constituent has first separated in certain parts. Possibly the pearly constituent re-crystallised on further cooling. Dr. Sorby observed in samples of grey iron a greater or less number of small ruby or deep-blue crystals, which may be silicon, or nitride of titanium.

The structure of white cast-iron is entirely different from that of grey iron, not only by the almost total absence of graphite, but in the feathery crystalline structure similar to that often seen in crystallised iron slags, with here and there patches similar to those of hard cast steel, and a few small laminae of graphite. The above-mentioned feathery crystals are intensely hard. In spiegel-eisen, or white cast-iron containing manganese, the large crystalline plates so characteristic of that substance are similar in character to the intensely hard compound in white iron, though differing in chemical composition. The rest is mainly the pearly substance, which crystallised after the hard material and forms the groundwork, together with an impure final residue.

The structure of spiegel-eisen is naturally very large, the crystalline plates being sometimes measured by

[1] Sorby, *Jour. Iron and Steel Inst.*, p. 277, No. 1, 1887.

inches. Dr. Sorby found that the true character could only be seen when magnified 200 diameters and upwards. About one-half of the bulk consists of an intensely hard compound corresponding to that of white cast-iron, though probably differing in chemical composition. The rest is mainly the pearly substance. The large plates are comparatively laminar crystals of the hard substance which crystallises out first; then over them, filling up the interspaces, is a mixture of the two constituents, having a very fine grain. The general structure consists of small, more or less parallel rods of the pearly substance, surrounded by a residue of the hard compound, so that, according to the direction in which the section cuts the groups of crystals, the are seen as parallel bars, or as a network with more or less elongated meshes, which vary in size from $\frac{1}{500}$th to $\frac{1}{3000}$th of an inch in diameter.

The various constituents of different kinds of cast-iron may be classified thus:

1. Iron free from carbon.
2. Carbon as graphite.
3. The pearly constituent.
4. The intensely hard compound.
5. The small ruby or dark crystals.
6. The impure residue.

§ 28. Fig. 8 shows a sample of grey pig iron cut from a square bar in transverse section. The most noticeable features are the irregular patches of ferrite and the edges of the plates of graphite, which appear to have arranged themselves with the broad surfaces parallel to the cooling surface and at right angles to the cross section. They lie in all directions, for the most part in straight lines, crossing each other and breaking up crystals of ferrite into mere irregular patches. The only uniform structure in the whole mass is the groundwork of granular pearlite, with its characteristic pearly

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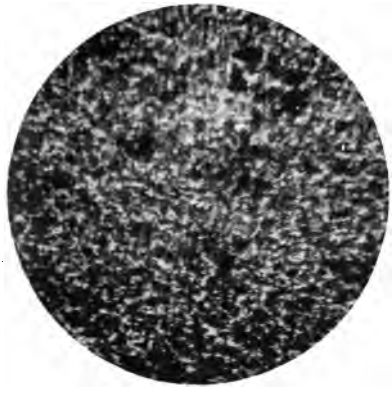

FIG. 9. Grey pig iron, longitudinal section. ×50 dia.

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FIG. 10. White cast iron. ×50 dia.

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FIG. 11. Cast iron with 2% manganese, quenched in water. ×200 dia.

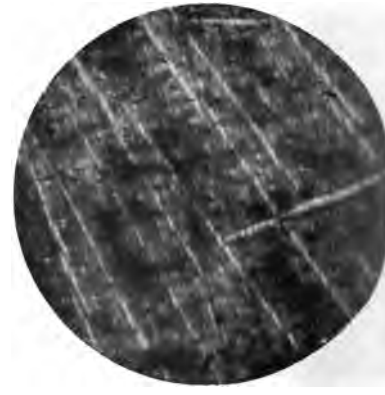

FIG. 12. Cast iron with 2% manganese, cooled slowly. ×50 dia.

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lustre, rendered more iridescent by the etching liquid, which was dilute nitric acid. Fig. 9 shews a longitudinal section from the same bar. It exhibits a much more heterogenous structure, and the crystals of graphite are less clearly defined, but massed in what is better represented by patches, the edges of which fringe off into the groundwork. The crystals of ferrite apparently occupy a larger portion of the surface and the pearly areas are more restricted. In grey cast-iron, as in other varieties of iron, the crystals are smaller when the cast specimen is of small dimensions. This is especially the case with the crystals of graphite, which are then so small as to form a confused heterogenous mixture of small crystals, with only imperfect definition. In all cases a very much better idea can be obtained of the structure by viewing the section in the microscope than by the inspection of a photograph of the same. Indeed, to get a proper idea of the nature of any sample, it must be viewed under different powers, beginning with a low power and finishing with a high power.

When grey cast-iron solidifies and cools it crystallises, and, as Sorby remarks, it is almost certain that graphite is the first to crystallise, then the ferrite, and lastly the pearlite, which, being the last to solidify, is likely to contain most of the combined carbon and impurities. This therefore acts as a kind of cement, binding the crystals of graphite and ferrite together. The slower the cooling the larger these crystals will be, and, if the metal is disturbed during this crystallisation, the cement being liquid or soft, they will have little cohesion, and the iron will be weak. At a lower temperature the disturbance is much less important, because the cement has become consolidated; and the crystal grains being now fixed, a much greater force is required to overcome the cohesion. The larger the grains, however, the less coherent are they likely to be, owing to the larger area of the cleavage planes. If, instead of cooling slowly, the

iron is cooled rapidly by chilling the growth of the crystal grains is checked, and tends therefore to produce a fine-grained structure; and, if the silicon is low, little evidence of graphite crystals will be observed, and the iron, instead of being carbonless (ferrite) will be chiefly in the form of cementite.

All shades of difference exist between the very greyest and the very whitest pig irons, the iron in the former being almost entirely ferrite, and in the latter almost entirely cementite, either free or as pearlite and martensite, and as the hardness depends on the condition of the carbon and the allotropic condition of the iron, all shades of hardness will also occur between very grey and very white pig irons. In order to keep the issue clear, reference to the disturbing influence of foreign elements has been omitted here. Evidently, in grey cast iron the pearlite cement is the hardest constituent, although in the crystallising stage it is soft and plastic, but as it cools it gradually gets harder, hence the smaller the proportion of pearlite and the larger the crystals of ferrite and graphite the softer will be the iron.

Now, if white cast iron, when free from disturbing elements, such as phosphorus, is gradually re-heated, the carbides are gradually decomposed and dissociated, with the formation of graphite and ferrite, the crystals of which grow larger as the time and temperature is increased up to a certain limit, and the iron becomes grey and malleable. If, however, the temperature be raised too high, so as to approach the melting point, the pearlite cement becomes too soft to hold the crystals firmly, and they become less coherent, with a subsequent weakening of the whole mass, so that it becomes brittle instead of malleable.

§ 29. The structure of white cast iron after chilling is represented in fig. 10. The general appearance, under low powers, is that of fern-like bodies, covering almost

the whole surface, and formed of long rectilinear needles with a number of transverse spines at right angles, each forming a skeleton, on which it is conceivable, under favourable conditions, that perfect crystals might be developed. These crystallites are embedded in a dark groundwork, probably of pearlite, which occupies a very subordinate portion of the surface, but the relative proportions vary from place to place. On examination with the higher powers the characteristic structure of martensite is abundantly in evidence. A network of large mesh, each enclosing a considerable area, may also be observed, as though a small amount of cementite was present. This may be, however, due to the presence of impurities which segregate in this mesh and set up planes of weakness. The large proportion of martensite readily explains the great hardness of white cast iron, with its accompanying brittleness. Now, white iron may be obtained from iron and carbon alone, but as this never happens, except in laboratory experiments, the whiteness is generally due to foreign elements, such as sulphur and manganese, which keep carbon in the so-called combined form and therefore prevent the separation of graphite. In making chilled castings an iron low in silicon and comparatively high in manganese is very desirable for the reasons mentioned above.

To show the effect produced when pure iron is heated with charcoal, Saniter[1] heated a piece of iron wire, 0·04 inch diameter, in a porcelain tube with charcoal, for varying periods, to a temperature of 900° C., and after being allowed to cool in the tube a portion was removed for analysis, with the following results: After 7 hours it was found to contain 1·64 per cent. of carbon, and after 14 hours this amount was increased to 2·79 per cent. Microscopic examination revealed the fact that pearlite with bands of cementite extended in all directions to the surface. After twenty-one hours' heating

[1] *Jour. Iron and Steel Inst.*, 1897, No. II., p. 122.

the total carbon was 2·95 per cent. and consisted of pearlite, cementite, and graphite, although the latter could not be detected under the microscope. The cementite was segregated towards the centre, none of the bands extending to the exterior. The surface of the wire was coated with graphite, which was carefully removed before analysis. Baron Juptner [1] concludes from the above, and similar experiments by other observers, that in the neighbourhood of 1000° C. graphite is not the most stable form of carbon, and that :

Mixed crystals + graphite = martensite + cementite.

He assumes that absorption of carbon by iron at the above temperature is accompanied by the formation of martensite. In such cases where the martensite does not come into immediate contact with the carbon, as in the interior of the mass of iron, or in such parts of the surface where the charcoal does not touch the iron, the separation of cementite occurs. Theoretically we may conceive of the continuation of the carburisation until the carbon is wholly in the form of graphite and cementite, but with an increase of temperature the cementite is dissociated until we get martensite and graphite, at which temperature graphite is more stable than the carbide.

§ 30. The general influence of manganese on cast iron has been already explained, and it has been shown that manganese has a tendency to make the iron white and hard. In all probability manganese and iron form isomorphous mixtures, and each is capable of combining with carbon to form similar compounds. Thus cementite, $Fe_3C$, is the analogue of manganese cementite, $Mn_3C$, and these may unite to form a double carbide $(Fe\ Mn)_6C_2$. Similar compounds of iron and manganese with silicon also probably exist, as in the case of silicon-

[1] *Jour. Iron and Steel Inst.*, p. 232, No. I., 1901.

spiegel-eisen. If this view is correct, then the pearlite, etc., of manganese steels also contains carbide of manganese, and the formation of such double carbides may explain the great hardness of manganese steels.

Fig. 11 shews a sample of white cast iron containing 2 per cent. of manganese cooled in water. The structure, as seen in a polished surface, is compact, but when the piece is broken it presents a highly crystalline fractured surface, the crystals being arranged with their broad surfaces at right angles to the cooling surface. After etching the polished surface in dilute nitric acid, or in iodine solution, and examining under the microscope with a fairly high power, two prominent structures present themselves. The groundwork is evidently pearlite, which forms a number of crystal grains of irregular shape, and standing out from this are white masses, which are not homogeneous, but having a more or less striated appearance, the striae running in a direction roughly at right angles to the general length. The white parts are not discoloured by the etching liquid, but the ground-mass is turned brown. Both portions are very hard, but the white portions are the hardest, from which it may be inferred that martensite, or its manganese equivalent, is abundantly present.

Fig. 12 shews a portion of the same metal, containing 2 per cent. of manganese, as above described, but allowed to cool slowly. The general structure is that of a very fine network of a pearlitic nature, and which seems to be the hardest constituent, and has been formed during the slow cooling, for it is not present in the quickly cooled sample, and may be a variety of martensite. The ground-mass is dark, of which only a comparatively small portion of the surface is visible, but here and there patches of material of the same colour have segregated, forming circles, and have superimposed themselves on the fine network. A series of white, structureless bands, of singularly uniform width, and

which have probably crystallised before the general network, cross the surface and each other at all angles. They are evidently the edges of large crystalline plates which appear to occupy about one-third of the mass. The before-mentioned circles and patches cover these bands as well as the network. The crystalline plates are very hard, and as they show no structure when magnified to 300 diameters, they are probably chemical compounds of iron and manganese with carbon and possibly silicon.

# CHAPTER VI.

## WROUGHT IRON.

§ 31. This term is practically applied to iron produced by puddling pig iron, hammering, rolling, reheating, and finishing the product by hammering and rolling. By these mechanical operations the structure of the iron becomes fibrous, tough, malleable, ductile, and highly tenacious. Now, iron in its natural state is said to be granular, but on microscopic examination it is found to be crystalline, therefore the fibrous condition is not inherent but purely artificial, with a constant tendency to pass back again to its normal state, which is considerably accelerated by the presence of certain impurities, especially those which readily induce a crystalline state.

Wrought iron contains about 0·05 to 0·1 per cent. of carbon, and a considerable amount of slag, which is drawn out into long fibres by the rolling process, and appears as black lines when seen in a longitudinal section, and as black patches when viewed in a transverse section. It is these slag threads and not the iron which give the fibrous appearance to wrought iron. Dr. Sorby says the ultimate crystalline grains of iron exhibit but little distortion or drawing out, but when very much slag is present, so as to separate the particles of iron to a considerable extent, the distortion of the iron becomes

greater. On the other hand, when the amount of slag is small, the iron grains are little, if at all, longer in the line of their length than in the line of their thickness. As far as the iron itself is concerned, there is very little difference in the appearance of longitudinal and transverse sections. There is every reason to believe that the separate grains of iron are imperfectly developed crystals, and this crystallisation often takes place after the iron has been hammered or rolled, but is still hot. This crystallisation is probably due to a strong tendency in distorted crystals to recover their normal shape, and to be restored to the condition of stable equilibrium. Though the crystalline grains in wrought iron are of irregular form, they fit closely together in every direction. We may, however, conclude that the cohesion between contiguous crystals is less than that of portions of the same solid crystal. This explains why, when suddenly broken, the crystals are separated in such a manner as to give rise to a so-called crystalline fracture, whereas, if broken more slowly, so that they may be drawn out and distorted before separating, a fibrous appearance may be produced.[1]

It is a generally recognised fact that wrought iron when submitted to constant vibration becomes what is termed crystalline, and more brittle. Now, if the crystalline nature of wrought iron be such as is represented in the preceding paragraph, it follows that vibration cannot make the metal crystalline, because it already is in that condition, and some other explanation of the change must be advanced. It is conceivable that the effect of vibration is to tend to dislocate the joints of the individual crystals, which have been assumed to be the weakest parts. But some may be assumed to be weaker than others, and these planes of weakness would be the first to yield to shock. One crystal after

[1] Dr. Sorby, *Journal of Iron and Steel Inst.*, p. 265, No. 1, 1887.

another becomes disarranged, until finally the whole section may be in such a condition of weakness as to break asunder when an additional shock is imparted. It is doubtful, however, whether iron of high quality, containing the ordinary impurities in small amounts, especially when the phosphorus is practically absent, ever succumbs to the shock of repeated vibrations, however long the action may last, because in that case there is no reason why one junction between two crystalline planes should be weaker than another, and, if rupture occurs, all the junctions must simultaneously give way, which is extremely improbable. It necessarily follows that weakness in bar iron which has been properly manufactured, and containing only the normal quantity of slag, must be due to the presence of impurities, some of which, it is well known, have a much greater weakening effect than others. If, as Dr. Sorby considers, recrystallisation occurs on cooling from a high temperature, a molecular disturbance is brought about which is complicated by the nature and amount of impurities present.

It is another well-authenticated fact that iron becomes stronger and tougher by repeated forging up to a certain point, which tends to close up vacant spaces and bring the crystalline planes into more intimate contact. The iron becomes more uniform and closer in grain, the slag threads become thinner, and the iron crystals smaller. One can easily understand that such treatment, by making the structure more uniform and obliterating irregularities, produces greater cohesion, but it also tends to show that a large crystalline structure is weaker than one in which the crystals are more numerous, and presumably the points of contact between the particles greater. It is recognised that a coarse structure is generally an indication of weakness, and that this kind of configuration is often brought about by the presence of impurities, which tend to produce larger

crystals, although the opposite is sometimes the case. Probably in cases where a foreign element does not materially interfere with the properties of a metal, it is because that element produces crystals isomorphous with those of the metal in which it is dissolved, as in the case of manganese in iron.

Crystalline structure is so often an indication of brittleness in metals that an ordinary person naturally associates this property with minimum strength. But a little reflection will show that this is an unjust assumption, for it is well known that a bar of iron when broken may show a crystalline, or what the workman calls a granular appearance, and yet forge and work well. Moreover, it has been shown that iron is naturally crystalline, and yet it is an exceedingly malleable and ductile metal. Now, if the mass of a piece of iron is workable, it is highly probable that the individual crystals are the same, and that the properties of the mass are the sum of the properties of the component crystals. In fact, the crystals of one element may be malleable and those of another just as brittle; in other words, some crystals are malleable and others are less so, varying with their nature. The same is true of the crystals of compounds or alloys of two or more elements.

As wrought iron is made up of two principal constituents—iron and slag, and as the proportion of the latter is variable, as well as its mode of distribution through the mass, it follows that one sample may contain much more slag than another, and that the size and shape of the crystals of iron may vary accordingly. Now, the mode of production of wrought iron, the manner in which pig iron is purified and the subsequent mechanical treatment to which the iron is subjected do not tend to the regular and ordinary arrangement of the component crystals, and this heterogenous condition is still further intensified by the presence of slag, which

has been shown to be much more plastic than that of iron at a high temperature. The crystalline planes are not therefore always in that perfect contact which is consistent with great strength, and some kind of cementing matter must be present to occupy the vacant spaces and bind the whole firmly together. This cement is probably what is now known as pearlite, an intimate mixture of iron and iron carbide. Wrought iron is not therefore simply iron and slag, but would seem to require in addition a certain amount of carbon to produce the necessary cementing material, and if this be so, combined carbon is as essential to wrought iron as it is to steel, a view which is not generally recognised.

On bending a bar of iron the convex surface is stretched and drawn out into threads or fibres, while on the concave side the metal is much contorted and puckered. If the bar is bent back again it easily breaks. In this case the crystalline arrangement is disturbed and the particles are in a state of chaos, the horizontal direction being changed to a vertical one without the power to cohere, and probably some of the crystals themselves are broken through. A somewhat similar arrangement occurs when a bar of iron is twisted until it breaks, but in this case the particles are forced diagonally and the gradual change is more readily followed.

Wrought iron, when viewed under the microscope with a low power, seems to consist of white patches, with streaks or blobs of slag, according as the section is a transverse or longitudinal one, and also as the specimen has been taken from a rolled or hammered bar. As regards the iron itself, there is very little difference between a transverse and a longitudinal section, and the individual crystal grains are very much smaller than those of pure iron allowed to cool slowly. Although little actual distortion of the separate crystal grains takes place by the mechanical treatment of wrought

iron, there is reason to believe that such grains tend to arrange themselves end to end in the direction in which the metal is forced to flow in the rolling process, and probably that recrystallisation takes place at a certain temperature in cooling, which would tend to neutralise any distortion conferred by rolling, etc. Of course, microscopic evidence is not so important in the case of wrought iron as in steel, because the character can be fairly accurately judged by inspection of the fractured portion of a bar or sheet. Nevertheless it may be useful to see and know the cause of certain defects which arise from time to time, and to properly apportion the blame to the right cause.

The general nature of wrought iron has been already discussed, and the following sections will indicate the appearance of polished and etched specimens under the microscope. Fig. 13 shews a sample of ordinary wrought iron of good quality when magnified to about 50 diameters. The relative proportions of iron and slag will vary not only with different samples but also in different parts of the same piece. Even with the naked eye it is easy to see the compression which the metal has been subjected to, by the general massing and wavy appearance of portions of the surface, but it is only when the section is highly magnified that the true nature of the structure is revealed. It consists of blobs of brown-coloured, structureless slag embedded in a very fine network of crystal grains of iron, the boundaries of which are probably formed of carbide of iron. In another sample which I have before me the crystal grains of iron are barely perceptible, the section appearing to consist of a white wavy ground-mass of iron in which are irregular patches and strings of slag.

Fig. 14 shews a longitudinal section of good quality wrought iron. It contains comparatively little slag, and the crystal grains of iron differ but little in shape from the transverse section, but the slag is arranged in

FIG. 13. Wrought iron, transverse section. ×50 dia.

FIG. 14. Wrought iron, longitudinal section. ×50 dia.

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FIG. 15. Pure iron. ×50 dia.

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FIG. 16. Dead soft iron. ×50 dia.

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Main

patches with the longer axes in the direction of the length of the section. A number of small blobs of slag are also present, as though the rolling had pulled the slag asunder, leaving portions distributed among the crystals of iron.

# CHAPTER VII.

## STEEL.

§ 32. Steel is iron with which is associated carbon and small quantities of other elements in combination with each other and with the iron. It is capable of being hardened to a high degree, and is malleable, ductile, and tough. It includes primarily compounds or alloys of iron with from about 0·2 to 1·8 per cent. of carbon, and compounds or alloys of iron with carbon and chromium or manganese, nickel, tungsten, etc., all of which possess great hardness and toughness. The great distinguishing features of steel are the properties of being hardened by sudden quenching from a high temperature, and tempering by raising the hardened steel to 200° or 300° C. The term steel is also erroneously applied to iron containing less than 0·2 per cent. of carbon, and which cannot be hardened by sudden quenching. The expression "mild steel" is then applied to such metal so as to distinguish it from steel proper. If the same quality of metal were made by puddling or weld processes then it would be termed iron. The mere fact of melting and pouring it into an ingot makes it steel, according to the popular notion. It must be however conceded that ingot metal is practically free from slag and differs structurally from weld or wrought metal. When another metal is present as a prime constituent it is

customary to designate the steel with the name of that metal prefixed, hence we get the terms manganese-steel, tungsten-steel, chrome-steel, etc. In contradistinction to mild steel, the term hard steel is applied to those varieties rich in carbon, and medium steel to those intermediate between mild and hard. Other names given to steel are such as Bessemer steel, Siemens steel, open-hearth steel, crucible steel, etc.

With regard to the constitution of steel, Howe says,[1] "I conceive it to consist of a matrix of iron (which is sometimes comparatively pure, as in ingot iron and annealed steel, and sometimes chemically combined with a portion or even the whole of the elements present, probably in indefinite ratios), and a number of independent entities, which we may style 'minerals,' chemical compounds of the elements present, including iron, which crystallise within the matrix, and by their mechanical properties, size, shape, and mode of distribution also profoundly affect the mechanical properties of the composite mass, though probably less profoundly than do changes of corresponding magnitude in the composition of the matrix."

Steel, with its mineral components, may be likened to a rock, such as granite, which consists of quartz, felspar, and mica, all of which unite to form a uniform mass when the granite is melted, and, if allowed to cool quickly, this homogeneous nature is maintained, but, if made to cool very slowly, separate minerals crystallise out, the first one to form occupying the dominant position. Now, steel contains at least three well-marked constituents which can be readily recognised, viz., iron, termed ferrite; iron carbide, termed cementite, having the formula $Fe_3C$; and an intimate mixture of the two, generally arranged in parallel striae, termed pearlite. If highly carburised steel is long exposed to a certain high temperature, graphite

[1] Howe, *Metall. of Steel*, p. 2.

separates out and the steel will consequently have a coarse structure. If such steel is cooled slowly from a strong red heat the carbon separates as a definite carbide, $Fe_3C$. If the steel is strongly heated and rapidly quenched in cold water, no carbide or graphite separates, and the carbon is in the condition known as hardening carbon or martensite.

These variations in the condition of the carbon in steel modify the action of different solvents, so that polished sections placed in suitable liquids have the component minerals revealed, because they are acted upon unequally, and some of them not at all. In some reagents, such as infusion of liquorice-root, or tincture of iodine, one constituent is coloured, while another remains unaltered. If the solution is a powerful one, such as strong nitric acid, all may be acted on together and simply a roughness produced. Another important factor, which has already been alluded to, is the condition of cooling. By slow cooling a coarse structure is generally produced, and by quick cooling a finer structure. If the steel is heated sufficiently strongly to produce a coarse structure, then vigorous hammering during cooling will produce a finer structure. The amount of work which has been put on the steel determines to some extent its strength, and therefore its structure, the former property depending on the external condition of the metal for the same composition. The relative influence of silicon, manganese, sulphur, and phosphorus on the proportion of the combined carbon which passes into the cement and the hardening conditions respectively has not yet been accurately determined, it is probable that they form ternary or even more complex compounds with the iron and carbon, so that the latter may not be either in the cement or in the hardening form as now understood.[1]

[1] A valuable paper by Mr. Stead on the effect of phosphorus on iron will be found in *Jour. Iron and Steel Inst.*, No. 2, 1900.

Steel may be said to be capable of existing in three distinct states: (1) In the soft form, produced by strongly heating and allowing to cool very slowly. Steel is then in its softest and toughest state, due to the release of strain produced by hardening or mechanical stress. (2) Hardening is effected in steel with upwards of 0·3 per cent. of carbon by raising it to a strong red heat and plunging it into some liquid capable of cooling it rapidly; and the relative degree of hardness will depend upon the rate at which a given liquid conducts away the heat. The temperature to which the steel is raised must be higher than the recalescence point. The effect of hardening is to increase the hardness, raise the elastic limit, generally to increase the tenacity and diminish the ductility.

The cause of hardening is attributed by different authorities to different conditions. The general explanation for a long time was that the sudden cooling preserves the condition of the steel in which it exists at a high temperature, and especially that of the carbon. Another explanation states that the hardness is due to the unequal stresses set up by the outer layers cooling much quicker than the interior, and by the compression of the exterior the superficial density and hardness is increased. Akerman suggested that the hardening is due to the compression, caused by sudden cooling, forcing the carbon into the hardening state. Osmond has introduced and stoutly supports an allotropic iron theory. If a bar of unhardened steel be heated to 800°C. there are stages where the cooling is not uniform. This is probably due to molecular change in the steel, which produces or absorbs heat. These critical points may be observed with great accuracy by means of the Le Chatelier pyrometer.

Osmond considers that iron assumes two or more allotropic forms, viz. *alpha* iron, which exists in soft iron and steel, and is itself soft and malleable; *beta* iron, which is

hard, strong, and brittle, and which exists in hardened steel. He states that one variety changes to the other at certain critical temperatures. If carbon and other elements are absent, these changes occur rapidly; and however quickly pure iron is quenched from a high temperature, it is not too quick to prevent the change. But if carbon is present it impedes the change, and, if the steel is rapidly quenched, may totally prevent it, thus keeping the iron in a hard form. In mild steel the amount of carbon is insufficient to prevent the change; hence the steel is not hardened. In cold working it is also assumed that the soft form of iron is changed to the hard modification.[1] Howe considers that the modifying effects produced by cold working are too great to be referred to mechanical action, and, as the carbon does not change, the iron must change allotropically. He suggests that hardening is not due to "beta" iron alone, carbon acting only as a heater, but to a combination of beta iron with carbon. He calls this the "carbo-allotropic" theory. Hardening then, according to this, is due chiefly to the preservation, by sudden cooling, of a hardening carbide of "beta" iron, of perhaps varying composition; and, secondly, to intense residual stress.

3. Tempering consists of the gradual re-heating of steel up to a certain temperature below a red heat, so as to release the tension induced by the sudden cooling. Some carbide is set free, the metal loses its brittleness and becomes softer in proportion to the temperature to which it is raised. By this means various degrees of hardness may be retained in the same steel to suit the requirements of different articles. The surface of the steel is made bright before heating, and when the temperature reaches 220° C. a pale yellow colour appears, succeeded by other colours as the temperature rises, so that the colour roughly indicates the temperature of the steel, and therefore the degree of softness or

[1] *Jour. Iron and Steel Inst.*, 1895.

temper. The following table shows the tempers used for various articles, the lowest temperature indicating the hardest temper:

| Temperature. | Colour. | Article. |
|---|---|---|
| 220°C. | Pale yellow. | Surgical knives. |
| 230° | Straw ,, | Razors. |
| 255° | Brownish ,, | Scissors, hard chisels. |
| 265° | Purplish brown. | Axes, planes. |
| 277° | Purple. | Table knives. |
| 288° | Light blue. | Swords, springs. |
| 293° | Dark ,, | Fine saws, augurs. |
| 316° | Blackish ,, | Hand saws. |

The term "temper" is used to express the hardness whether due to treatment or composition.

The effect of different elements on steel or iron-carbon alloy is widely different. Manganese, for example, hardens steel very vigorously. Steel with upwards of 12 per cent. of manganese shows no break in the cooling curve, and is assumed to prevent hard beta iron from passing into the soft alpha variety. It also is not susceptible to magnetism. Chromium has the reverse effect, as it is assumed to enable the hard beta iron to pass into the soft alpha form at a higher temperature than would otherwise be the case, and this may explain the intense hardness of chrome steel when suddenly quenched from a high temperature.

§ 33. **Manganese Steel.**—Next to carbon, manganese is the element which plays the most important part in influencing the properties of steel, and when present in quantities up to 0·5 per cent. is highly beneficial, some of the best steel being that containing manganese. Steel containing 2·5 to 7 per cent. of manganese is brittle, but when the amount exceeds 7 per cent., alloys possessing great strength and toughness are obtained. A sample of forged material containing 14 per cent. of manganese and 0·8 per cent. of carbon seems to be the strongest alloy. When this manganese steel is plunged

at a red heat into water, no hardening effect takes place like that of ordinary steel, but the metal acquires increased tenacity and toughness. The higher the temperature of the steel and the greater the rapidity of cooling, the higher is the tenacity, toughness and elongation. In its usual condition it is very hard and easily scratches ordinary steel. Manganese steel does not exhibit the anomalous expansion and "after-glow," termed *recalescence*, which takes place in magnetic metals when they cool from a strong red heat down to a certain critical temperature.'[1]

§ 34. **Nickel Steel.**—This is steel with varying amounts of carbon, to which nickel is added in quantities of 1 to 3 per cent., and higher qualities containing upwards of 20 per cent. It seems to diminish the tendency of the metalloids to liquate, and therefore to produce a more uniform structure. It increases the elastic limit and breaking stress considerably. Steels rich in nickel are practically non-corrodible, and are among the most powerful connected with magnetism. They also possess a high elastic resistance. With over 25 per cent. of nickel, the steels are reversible as regards magnetism.

§ 35. **Molybdenum Steel.**—With 1 to 2 per cent. of molybdenum the steels are whiter than iron, very hard, brittle, tenacious, and possess a granular fracture, and in many respects resemble tungsten steels; but the latter generally show minute cracks, while the former have a perfectly smooth surface. Rapid quenching from a strong red heat has more influence on molybdenum than on tungsten steels.

§ 36. **Chrome Steel.**—Iron and chromium have a strong affinity for each other, and appear to form alloys in all proportions. Steel with 12 per cent. chromium and 1·8 per cent. carbon may be forged. It possesses a high

[1] Hadfield, *Inst. Civil Eng.*, 1888.

tenacity and a great resistance to pressure; the steel is harder to file and work in proportion to the carbon present. Hardened steel containing chromium has a very fine grain, and breaks with a vitreous fracture. It cannot be welded, it burns when highly heated owing to the strong affinity of chromium for oxygen. The addition of 0·3 per cent. of chromium and a like amount of molybdenum to steel greatly increases its resistance to penetration without making it brittle.

§ 37. **Tungsten Steel.**—This steel is highly valued for cutting tools and for magnets. It is known as Mushet's special steel. It possesses a natural hardness of its own, and when 3 per cent. and upwards are present it is actually softened by water quenching. Such alloys are difficult to forge, and cannot be welded. Tungsten imparts to steel a very fine and uniformly crystalline structure, and is very little affected by the atmosphere; it also raises the melting point considerably.

§ 38. **Molybdenum, Chromium, and Tungsten Steels.**—Alloys of pairs of these metals with iron have been made by De Beuneville.[1] In tungsten-chromium iron there is conclusive evidence that the iron alloys itself in preference with chromium. The same result occurs with molybdenum-chromium iron. The carbon is present in different forms. In one example the carbon was considered to be present in three forms: (1) Given off as an ill-smelling hydrocarbon by the action of dilute acids; (2) Carbon present in the residues obtained by acting on the alloys with bromine, which residues were not attacked by dilute hydrochloric acid; (3) Carbon found in the prismatic crystals. In these ternary alloys is also found the more complex carbide of chromium, with iron and molybdenum, or tungsten. The hardness of these alloys is due to the formation of definite carbides.

[1] *Jour. Iron and Steel Inst.*, 1895.

§ 39. **Copper Steel.**—Ball and Wingham[1] found that copper increases the tenacity of iron, and that the simultaneous presence of carbon assists in the more intimate association of copper with iron. With 0·8 per cent. copper and 0·1 per cent. carbon the alloy is somewhat fibrous, but with more carbon and a higher percentage of copper the structure is highly crystalline and extremely hard. Copper and pure iron alloy in all proportions by fusing the two metals together, and there seems little tendency for any subsequent separation by liquation, but the presence of carbon limits the amount of copper that can be alloyed with iron, the maximum of 7·5 per cent. being the limit in grey pig iron with 3 per cent. of silicon, and 15 per cent. in steel, with 1 per cent. of carbon. In most copper-iron alloys some of the copper exists as globules suspended in the solid metal, being highest when the metal is cooled quickly, and lowest when cooled very slowly. Copper in cast iron is neutral as regards its influence in retaining carbon in the combined form, or in causing it to separate as graphite. In steel, copper seems to retard the formation of pearlite. With the same steels, differing only in copper, the copper-steel on rapid cooling contains more diffused carbide. On very slow cooling the amount of carbide seems about equal in both cases. Copper in high carbon steels seems to be fatal to ductility, but when less than 0·5 per cent. is present in mild steel it does not materially affect the mechanical properties.[2] Copper seems to retard corrosion in steel.

§ 40. **Aluminium Steel.**—Aluminium in steel is not used to form definite alloys, as in the case of nickel and manganese. Up to 1 per cent. it does not materially lower the freezing point of iron, but imparts to it much

[1] *Journal Iron and Steel Inst.*, 1889.
[2] Stead, *Jour. Iron and Steel Inst.*, 1901.

greater fluidity when melted, and thus enables it to form sounder castings. The quantities generally used for Siemens steel is 0·05 per cent., and for Bessemer 0·1 per cent., but in no cases should 0·2 per cent. be exceeded. Aluminium in much larger quantities produces hard, white, and brittle alloys.

§ 41. **Micro-Structure of Steel.**—Although iron containing 0·05 per cent. of carbon is sometimes termed very mild steel, if it has been melted and poured into an ingot mould, it is better termed malleable iron, inasmuch as it is not capable of being hardened by sudden quenching. With microscopic sections, however, there is no strict line of demarkation as long as an almost infinitesimal portion of carbon is present. A section of pure iron, when perfectly polished and etched in very dilute nitric acid, is seen to consist of polyhedral grains or crystals, probably interfering octahedra and cubes. Two distinct types are generally observed: (1) Smooth and bright areas, consisting of pure iron, and (2) Greyish rough areas with a mottled or wavy appearance, being more readily attacked by the acid. It is probable that the latter contain small amounts of carbon. As it is next to impossible to prepare perfectly pure iron, a little carbon is practically always present and in addition to the roughened appearance of some of the crystals, little portions of pearlite or cementite segregate between the faces of some of the crystals and form dark patches after etching.

Fig. 15 shows the structure of a sample of as pure iron as the author has been able to obtain. The iron was produced from pure crystallised ammonium—ferrous sulphate. The crystals were dissolved in water and the iron precipitated as oxide by ammonia. This was well washed, dried, and reduced in a hard glass tube by a current of pure hydrogen gas. The reduced iron was then melted in a small clay crucible, lined with

lime, and a lid carefully luted on. The whole was placed inside a larger crucible also covered with a lid, so as to exclude any carbon or carbonaceous matter. The pots were left in the furnace to cool slowly down. The iron was then faced and polished in the usual way, and afterwards etched in dilute nitric acid. In addition to the large crystals of ferrite, secondary crystals may develop during the cooling.

Fig. 16 shews a sample of the purest commercial sheet iron, known as "dead soft," and contains about 0·05 per cent. of carbon. It consists of large crystals of ferrite, showing the clear and rough areas as before mentioned. Little blobs, probably of cementite, also appear in places, and the junction lines of the crystals are thicker in some parts than in others, due to carbide of iron acting as a cement between the crystal grains. If this quality of iron is heated to about 700° or 800° C. and slowly cooled, the structure may be coarsely granular. On examining a polished and etched section the carbon will be found existing, not in areas or patches of pearlite, but in a state of massive cementite embedded in the ferrite.

Fig. 17 shews a sample of steel containing 0·15 per cent. of carbon, and made in a clay crucible, lined with lime and allowed to cool down in the fire. It will be observed to have the same general structure as the preceding one, but the crystals of ferrite are much more encroached upon by the matrix of pearlite, breaking them up into smaller grains. It will be seen from the foregoing examples that mild steel, say with less than 0·2 per cent. of carbon, presents a more or less crystalline structure, the size of the crystal grains depending on the treatment to which the steel has been subjected. A piece of steel is distorted by mechanical treatment and this mass distortion extends to the crystal grains, but on heat treatment such grains may be restored to their normal condition.

FIG. 17. Mild steel with 0·15% carbon, strongly etched. ×50 dia. Page 72.

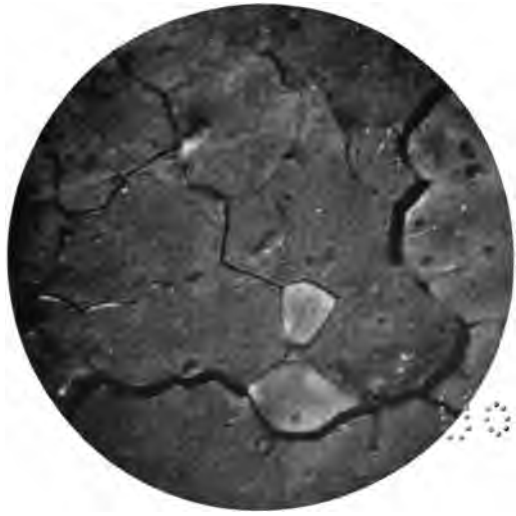

FIG. 18. Copper containing 1% bismuth, showing intergranular fracture. Page 73.

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§ 42. In some cases mild steel, after long annealing, exhibits a great tendency to become brittle. Such weakness may be due to two distinct characters:

1. When the line of fracture follows the junctions of the crystal grains. This is termed by Stead "inter-granular," that is, between the grains. The grains may not be in absolute contact, but separated by envelopes of substances that separate out when the metal solidifies or is slowly cooled. This defective junction may be often rendered more apparent by placing the section, face downwards, on the jaws of an open vice and striking with a hammer. The author has often observed the same thing when, after nicking with a chisel, a bar of metal screwed in a vice is forcibly broken by a hammer. The line of fracture invariably follows the direction of the inter-granular foreign matter. But the brittle envelope may be absent and the crystal grains perfectly united by cohesion, yet the metal may be weak. This is well illustrated in annealed steel containing phosphorus. Arnold explains this by assuming that the crystal grains contract unequally on cooling, leaving the junctions in a state of unnatural tension. Fig. 18 is a sample of copper containing bismuth showing inter-granular fracture.

2. The second character of weakness is when rupture is produced, not in the junctions between the crystal grains, but in the interior of the grains. This is due to cleavage. Now, by annealing, the crystal grains become larger and tend to arrange themselves symmetrically, several smaller ones uniting to make a larger one, which develops true cleavage planes and these become planes of weakness if such cleavage planes lie at right angles to the length or cross section of the bar, but if arranged heterogeneously the bar may have considerable strength.[1] Mr. Ridsdale[2] points out that re-heating of mild steel,

[1] *Jour. Iron and Steel Inst.*, No. II., p. 145, 1898.
[2] *Jour. Iron and Steel Inst.*, No. II., p. 107, 1899.

which had become brittle, to a temperature of 900° C., whether subsequently allowed to cool slowly or quickly, restores the toughness. Special stress is laid on rapid heating. Now steel, to a certain extent, bears its own history recorded in its structure, and steels of a given type possess certain characteristics in common, which can only be learned by studying a number of samples, and from these types other varieties may be studied and compared. The following classes are recommended:

Class I. Soft steel of normal composition after normal treatment.

Class II. Steel of normal treatment but of abnormal composition.

Class III. Steel of abnormal treatment but of normal composition, such as heating to a high temperature for a long or short time.

It is useful to remember that the size of the grain in normal steel is inversely proportional to the section area of the bar, and when it is not so, this gives an indication of the variation in the other conditions. The sections should be examined under oblique and vertical light. For defects, such as cracks, spills, blowholes, slag, segregations, etc., plain polishing is desirable. In some cases, heating to a straw colour may reveal their nature better. For internal structure the specimens may be uniformly etched by a solution of iodine in alcohol; while for deep etching a dilute solution of nitric acid is recommended.

Normal mild steel, on which work has been continued to below the critical temperatures, shows a uniform structure with small and ill-defined crystal grains, those at the edge being often smaller than those at the centre. If the steel has been heated too long, or at too high a temperature, yet not sufficient to burn it, the crystal grains will be larger at the outside than at the centre of the bar, due to the burning out of the carbon at the exterior. If the steel has been raised to a yellow heat and allowed to cool without work being done upon it

FIG. 19. Mild steel with 0·11% carbon, annealed for several hours at 700° C.

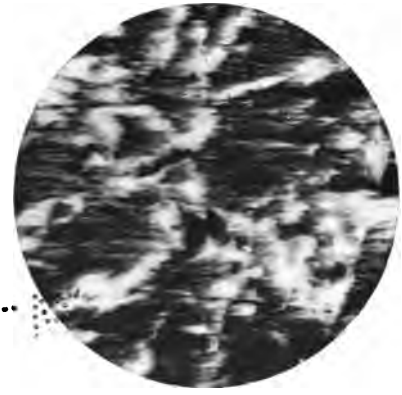

FIG. 20. Steel with 0·3% carbon. ×50 dia.

until it arrives at a blue heat, it becomes brittle, and flow-lines may be observed in various directions from the part where the pressure was applied, marking the direction in which the material has slipped; the metal, being in a strained condition, the flow-lines culminate in cracks.

Microscopic examination shows that steel at a blue heat is in a condition of peculiar sensitiveness, so that it readily retains the effects of shock or work. This is probably due to there not being sufficient heat for the strained parts to readjust themselves whilst cooling as is the case when work is finished at a red or white heat. It appears from the above that temperature is perhaps the most important factor in determining the brittleness or otherwise of steel. There is a temperature beyond which steel cannot be heated without being burnt, but there is also a temperature much below this which promotes brittleness. This temperature for mild steel is somewhere in the neighbourhood of 700° C., especially if the heating is very prolonged. The effect of continued annealing at this temperature is to considerably increase the size of the grain, which is generally an indication of weakness, but such brittle steel may be restored to its natural toughness by heating to 900° C. and allowing to cool slowly. These remarks only apply to normal steel of good quality, as with steel containing much phosphorus, say 0·2 per cent., re-annealing does not produce toughness although it changes its structure. Phosphorus tends to produce inter-granular weakness by the formation of a fusible phosphide. Fig. 19 shows steel with 0·11 per cent. of carbon, which has been annealed for several hours at about 700° C.

§ 43. In Fig. 20, containing 0·3 per cent. of carbon, the same general structure will be observed as in figure 17, but the pearlite areas are considerably extended,

and the ferrite has been reduced to an irregular amorphous mass, and partly immersed in the groundwork of pearlite, the latter being very distinctly marked when viewed with a high-power lens. With 0·6 per cent. of carbon the amount of pearlite has considerably increased and appears to cover a larger area than that of the ferrite. The pearlite is broad and well developed, showing its characteristic striated structure, some of which has probably penetrated the ferrite, imparting to it a mixed grey and white appearance, and destroying all resemblance of a crystalline form and making it more like a woolly than a crystalline structure. This variety of steel is shown in fig. 21.

§ 44. Steel containing 0·89 per cent. of carbon is composed entirely of pearlite, and is then at the saturation point for steel; and when the concentration of the carbide reaches a certain point, in consequence of the separation of the constituents which are in excess, both the carbide and the iron are isolated simultaneously at a constant temperature, forming pearlite. It is the solid eutectic alloy of one of the forms of iron, and of the carbide $Fe_3C$. The allotropic forms of iron have been already alluded to. Osmond considers it is the alpha modification of iron that unites with carbon to form the variety of cementite which is an essential constituent of pearlite, and he gives it the formula $Fe\alpha_3C$, whereas in hardened steel the iron of the carbide is present in the beta form with the formula $Fe\beta_3C$ as in martensite. Fig. 22 represents steel composed almost entirely of pearlite. It contains 0·9 per cent. of carbon, and is sufficiently magnified so as to bring out the striation. Fig. 23 shows the same after hardening.

§ 45. As the carbon increases beyond 0·9 per cent. the ferrite disappears, and is replaced by pearlite, so that the higher carbon steels, with more than 1·2 per cent. of carbon, are composed of pearlite and cementite.

FIG. 21. Steel with 0·6% carbon. ×200 dia.

FIG. 22. Steel with 0·9% carbon. ×200 dia.

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FIG. 23. Steel with 0·9% carbon, hardened. ×200 dia.

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FIG. 24. Steel with 1·2% carbon. ×200 dia.

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Not to be taken away

FIG. 25. Steel with 1·2% carbon, hardened. ×200 dia.

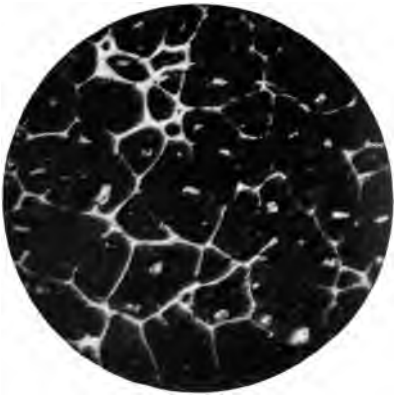


FIG. 26. Steel with 1·8% carbon. ×50 dia.

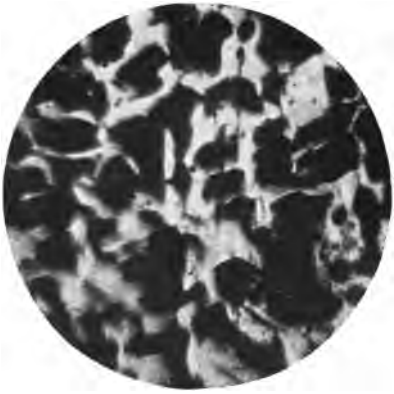


FIG. 27. Steel with 1·8% carbon, hardened. ×200 dia.

Steels containing more than 0·9 up to 1·2 per cent. of carbon are mainly composed of pearlite, if cooled sufficiently slowly. Fig. 24 shews the structure of cast steel containing 1·2 per cent. of carbon. It will be observed to have a striated appearance similar to that of the previously described sample, containing 0·9 per cent. of carbon. There appears to be an absence of cementite. Fig. 25 illustrates the same steel containing 1·2 per cent. of carbon after hardening. The pearlite has practically disappeared and a new substance appears as a consequence of the hardening process. The pearlite has changed to martensite, and along with this is an intermediate formation, softer than martensite, and of a more homogeneous structure, termed troostite. This is probably a consequence of the too rapid quenching, which does not allow sufficient time for the complete conversion of pearlite into martensite.

§ 46. Fig. 26 shews steel containing about 1·8 per cent. of carbon. It will be observed that a different structure to that of the preceding fig. 25 is developed. In consequence of the greater proportion of carbon the cementite has considerably increased and envelops the pearlite by an imperfectly continuous network. When this is still more highly magnified both the characteristic features of the pearlite and cementite are rendered more apparent. The discontinuity of the surrounding network is another evidence of the presence of cementite, which differs in this respect from ferrite. The ground-mass is pearlite.

Fig. 27 shews the same steel as above, containing 1·8 per cent. of carbon, but instead of being annealed has been hardened. It differs from the preceding figure in having a dark ground and an irregular brilliant white network with thick walls and occupying the greater part of the surface. The latter appears homogeneous in structure, and with moderate powers seems quite continuous. On

examination, however, with high powers the meshwork is penetrated by fine lines in various ways, as though the material of the groundwork had diffused into it. The groundwork is coloured dark brown by liquorice solution, while the above-mentioned white network is unaffected.

§ 47. Mr. Osmond has shewn that when a high carbon steel is heated above 1050° C., and rapidly quenched in iced brine, an irregular zigzag structure appears, and when such steel is examined under the microscope it is found to consist of two elements—a hard substance resembling martensite and a softer material, termed austenite, which appears to be non-magnetic. The density of steel containing much austenite is about as great as that of annealed steel, but on cooling in liquid air it becomes less. The hardness at the same time increases and approximates to that of martensite (see fig. 6). The relative proportion of austenite and martensite in quenched steel no doubt varies with the rapidity of cooling, for with water quenching in the usual way little or no austenite seems to be present. The formation of austenite depending on temperature, and the suddenness of the cooling preventing its dissociation, would seem to indicate that it is a product of the combination of carbon with that allotropic modification of iron which exists at temperatures above 1050° C., and termed gamma iron. A comparatively large amount of dissolved carbon seems to be necessary for its composition to be retained on quenching.

With respect to austenite, Mr. J. E. Stead[1] examined a sample containing 89 per cent. of iron, with about 8 per cent. of copper and 2·3 per cent. of carbon, and which had been slowly cooled. It contained free cementite in net-like formation, enclosing areas which, on polishing with sulphate of ammonia, yielded a

[1] *Jour. Iron and Steel Institute*, No. 2, 1901.

structure identical with the finest examples of martensite and austenite produced by Osmond. If austenite is formed and retained on cooling it is probably due to the large proportion of combined carbon.

§ 48. Professor Campbell of Michigan [1] has studied the carbides of iron in steel by dissolving the steel in hydrochloric acid and passing the gas evolved through bromine in order to convert unsaturated hydrocarbons of the general formula $C_nH_{2n}$ into their di-brom derivatives, $C_nH_{2n}Br_2$; the latter being then analysed and fractionally distilled for the purpose of qualitatively identifying the various constituents. From the percentage of bromine in the derivatives the average number of carbon atoms in the molecule were calculated. The following conclusions were arrived at, viz.: (1) That in annealed steel the average number of carbon atoms in the molecule decreases as the percentage of carbon increases; (2) that the effect of hardening seems to be to lower the number of carbon atoms in the molecule of derivatives and to increase the proportion of carbon escaping as gaseous paraffins; (3) from the percentage of carbon in the steels examined the annealed samples under 0·89 per cent. of total carbon must consist of pearlite with ferrite; while those above 1 per cent. consist of pearlite with increasing quantities of cementite.

The results obtained appear to indicate that there are several different carbides existing in steels, and that these carbides have different molecular weights. According to this view the formula $Fe_3C$ is merely an empirical one. The hypothesis offered by Professor Campbell makes the fundamental assumption that carbon forms with iron a series of compounds which might be termed ferro-carbons on account of their similarity to hydro-carbons. This series of ferro-carbons has the empirical formula $(Fe_3C)_n$, or $C_nFe_{3n}$.

[1] *Iron and Steel Inst. Jour.*, No. 2, p. 223, 1899.

In annealed steels containing less than 0·89 per cent. of carbon we should find the eutectic pearlite to consist of alternate laminae of $C_nFe_{3n}$ and of ferrite, $Fe_{21n}$. The latter may be regarded as the iron of crystallisation, the ferro-carbons occurring in pearlite having a higher molecular weight than those occurring as free cementite. When steel is heated above a certain temperature the ferro-carbons dissolve in the iron of crystallisation forming martensite, which may be represented by the formula $C_nFe_{3n} + Fe_{21n}$; or according to Professor Arnold the empirical formula $Fe_{24}C$. When the ferro-carbons of high molecular weight dissolve in their iron of crystallisation they probably begin to split up, yielding lower members of the series, this dissociation increasing with rise of temperature.

Against this assumption of the iron of pearlite being iron of crystallisation, it must be remembered that there is no proof that pearlite is a chemical compound, but that the iron is similar to the ice crystals in a solidified cryohydrate, the two structural elements being merely in juxtaposition, forming simply a mechanical mixture. There can, however, be little doubt that molecular alterations of carbon and iron take place at certain temperatures in heating and cooling steel, and that polymerised iron carbides are capable of existing under certain conditions, so that iron carbides play a much more prominent part in influencing the properties of solid steel than elemental carbon. It is quite possible that carbon does exist in molten iron in a state of simple solution, and that the molecules of such carbon contain not more than two atoms, and in all probability are monatomic; but, on solidification and cooling, carbides are formed, which cannot remain in solution at certain high temperatures unless the steel be somewhat suddenly quenched. On slow cooling this carbide falls out of solution as cementite. Now, if, in high carbon steel, on cooling from a high temperature, an iron carbide

FIG. 28. Steel with 4·5°/. silicon, deeply etched. ×130 dia.

solidifies it must be before the eutectic solidifies, and this carbide is probably austenite, which at a lower temperature passes into martensite.

§ 49. Mr. J. E. Stead has shown that silicon in combination with iron favours the formation of large crystals which may be developed by etching after being heated to 1000° C. and allowed to cool exceedingly slowly. Fig. 28 shews a sample of steel containing 4·5 per cent. of silicon. The polished surface has been deeply etched with a 10 per cent. nitric acid solution, and is said to be the most perfect crystalline structure ever developed by metallographic methods up to that time. Heating up to 1100° C. effected no structural change. The granular junctions remained exactly as before heating. Osmond and Arnold have shown that there is no arrest-point, or allotropic change in high silicon and aluminium steels at 850 to 870° C. There appears to be an allotropic change at 700° C., as they cease to be more than feebly attracted by a magnet at that point, but there is no crystalline alteration. On subjecting the above silicon steel to cementation no carbon was absorbed, as there is no iron free to combine with carbon at the temperature of the cementation furnace. Professor Roberts-Austen found only one critical point, at 703° C., with 4 per cent. silicon-iron.

§ 50. With regard to the crystalline structure of metals, Mr. J. E. Stead [1] very pertinently remarks that "granules and crystals should not be confused together, for, although a granule is built up of crystals, its external form is not that of any kind of crystals, as it takes its form from its surroundings. It is better to term such a "crystal grain." In carbonless pure irons and steels of fine grain, produced either by forging or heat treatment, the grains increase in size slowly at 500° C., and more rapidly at between 600° and 750° C.:

[1] *Jour. Iron and Steel Inst.*, p. 185, No. 1, 1898.

and it is possible by heating at about 700° for a few hours to develop granular masses of exceeding coarseness. The cause of this is due to molecular activity and the natural disposition for the crystals in contiguous grains to assume the same phase or axial relations with each other; and when this is brought about the boundaries between them cease to exist. If pure iron, made coarsely granular by heating to 700° C. at a dull red heat, is heated to 900° C. the granules will again become small.

"The granules in carbon steel, containing from 0·2 to 1·2 per cent. of carbon, do not grow by long-continued heating to 700° C., but increase in size with each increment of heat above 750° C. If, however, such steels are reheated between 700° and 750° C. the coarse structure vanishes, doubtless due to carbon and perhaps allotrophy.

"Steels, with 0·10 to 0·15 per cent. of carbon, containing the pearlite in widely separated areas, on heating and quenching from above 750° C. will not have the large ferrite grains taken up, and the carbon will not diffuse beyond the original areas; yet, when heated to 850° C. and allowed to cool down slowly, the carbon areas are found far beyond their original positions. Therefore, it is not only the change from cement to hardening carbon which causes the breaking up of the structure, but also the diffusion of the carbon after the change has been effected. Good open-hearth steel, with 0·23 per cent. of carbon, may be heated to close upon its burning-point without becoming brittle, and it only becomes truly burnt when intergranular separation is effected."

§ 51. **Cemented Iron.**—The process of cementation consists of exposing bars of malleable iron in contact with charcoal to a high and prolonged temperature, in closed vessels, from which the air is excluded. The product is termed blister steel. For mild heats the

furnace is fired for about eight days, for medium heats about nine and a half days, and for hard heats eleven days. After firing, the pots containing the steel are allowed fourteen days to cool down, and during the first portion of this cooling period the conversion is continued, because the temperature is above a red heat.

Different varieties of blister steel are made and named according to their degree of carburisation, which depends on the length of exposure to the action of the carbon. If air has gained access to the bars in the pot, they become rough on the surface and have a skin of iron, due to the oxidation of the carbon. When a converted bar has been submitted a second time to the cementation process, it is termed "glazed" bar. Exclusive of this there were usually six grades of blister steel; but as the first or mild temper contained only about 0·3 per cent. of carbon, it has been practically superseded by Bessemer and Siemens steels. In the lower grades the central core of the bar is either unaltered or has only taken up a very small proportion of carbon, so that while the outer portion may contain 1 to 1½ per cent. of carbon the central portion does not contain more than 0·1 to 0·2 per cent. In the higher grades the conversion goes right through, and the difference between the outside and the centre is small. In a mild heat the mean carbon content is about 0·5. In a medium heat it is about 1 per cent., and in a hard heat about 1·5 to 1·8 per cent. of carbon. Doubly converted or glazed bars may contain over 2 per cent. of carbon.

The microscopic structure of cemented iron is very characteristic, because the ferrite and pearlite of unsaturated carbon steels are well marked, and the cementite and pearlite of supersaturated steel are equally in evidence. In glazed bars the cementite segregates in large masses and streaks. In "aired" bars the decarbonised outer layer consists of ferrite

with streaks and blobs of oxide of iron. The ferrite crystal grains are comparatively large, and the boundaries contain what is probably irregular streaks of oxide of iron.

Fig. 29 shews a sample of cemented mild steel containing about 1·5 per cent. of carbon. It consists of masses of irregular shape having the structure of pearlite, as though the original crystal grains of ferrite had been filled with a new substance, or it may be that the cementite is in a state of incipient formation. On hardening the above sample the laminated groundmass became very pronounced, but the main portion of the section was occupied by white wool-like masses of a hard substance, as shown in fig. 30. It very much resembles austenite, and indeed this hardened specimen appears to be entirely composed of two distinct bodies, which are probably martensite and austenite, the former being brown after etching with liquorice solution, and the latter white and structureless. Fig. 31 shews a sample of cemented iron supplied by Mr. Stead and containing 0·8 per cent. of carbon.

§ 52. **Iron Alloys.**—Certain alloys of iron have been brought into considerable prominence of late years, and are now manufactured on the large scale for industrial purposes. They may be regarded not only as solidified solutions of the minor constituents present, but also as containing one or more definite compounds, formed by reaction in the liquid or pasty mass before complete solidification. And even below the main freezing point some of the compounds may remain liquid and crystallise, and separate as their own freezing points are reached, or, on separation, may hold in combination part of the solvent corresponding to water of crystallisation in certain salts. Again, constituents may be present which solidify simultaneously with the general mass of the solvent. Iron carbides unite with elements of

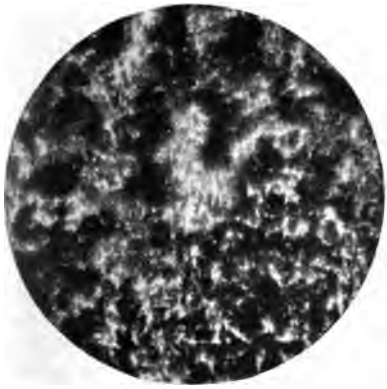


FIG. 29. Mild steel after cementation, 1·5% carbon. ×50 dia.

FIG. 30. Cemented mild steel, 1·5% carbon, hardened. ×50 dia.

FIG. 31. Cemented bar, 0·8% carbon. ×550 dia.

FIG. 32. Ferro-manganese, 80°/₀ manganese.
×200 dia.

FIG. 33. Silicon pig iron, with 10°/₀ silicon.
×50 dia.

high melting points, such as manganese, chromium, etc., which are for the most part hard, crystalline, and brittle.

§ 53. **Ferro-Manganese.**—This body doubtless contains in the mass of the alloy chemical compounds which take a definite crystalline form, and as the proportion of manganese diminishes to that in spiegel-eisen the characteristic platy structure is developed. Troost and Hautefeuille[1] have indicated that manganese forms with carbon and silicon definite compounds, which are exothermic, and probably manganese is much more energetic in forming compounds than iron, and has also a higher solvent power for carbon, thus forming indefinite solution compounds which readily pass from one form to another, such as from the broad platy forms of spiegel-eisen to the acicular and prismatic structure of ferro-manganese. In both ferro-manganese and spiegel-eisen a ternary compound is present. Fig. 32 shews a sample of ferro-manganese containing 80 per cent. manganese. The white masses are analogous to cementite, and probably have the formula $(MM^1)_3C$ where M represents manganese and iron in isomorphous compounds. The dark portion corresponds to pearlite, made up probably of ferrite and the double carbides of iron and manganese. Ferro-manganese may be described as consisting of heterogeneous masses, with constituents varying from the sharply crystallised compounds, prismatic or octahedral in form, to indefinite compounds analogous to vitreous silicates.

§ 54. Fig. 33 shows a section of silicon pig iron, containing 10 per cent of silicon. It has a large platy structure. The boundary lines of the plates are dark and very uneven in thickness, forming an irregular mosaic. The interiors are filled with fine striations, giving an iridescent appearance, the whole resembling grey pig iron.

[1] *Ann. de Chimie et Phys.*, vol. ix., p. 56.

§ 55. Fig. 34 shews a section of ferro-tungsten containing 28 per cent. of tungsten. It consists of a fine granular matrix, over which is distributed a closely packed mass of very irregular-shaped crystals somewhat resembling martensite. Dark spongy masses have segregated in parts of the section, but these are not likely to be graphite.

§ 56. Fig. 35 shews a section of ferro-chrome containing 20 per cent. of chromium. The mass is confusedly crystalline with drusy cavities here and there filled with acicular crystals. As chromium greatly increases the power of the alloy in taking up carbon, there is not likely to be present any free iron or chromium, so that the prominent crystals are probably carbides of iron and chromium in a fine grained matrix of a granular appearance, which is probably an eutectic mixture.

§ 57. Fig. 36 shews a sample of ferro-nickel containing 52 per cent. of nickel. It bears a close resemblance to high carbon steel, with its boundary lines of cementite, enclosing pearlite. From this it may be inferred that nickel forms with iron isomorphous compounds, and the boundary planes are composed of a double carbide of iron and nickel, while the interiors consist of a nickel-iron alloy, intimately mixed with the double carbides to form the eutectic mixture.

§ 58. **Slip Bands.**—Messrs. Ewing and Rosenhain[1] have investigated the microscopic structure of metals when the metal is subjected to strain. For this purpose polished surfaces were examined under the microscope while the metal was gradually extended until it broke. In this way a particular group of crystal grains could be continuously observed while the metal was being stretched. It was found that when a piece of iron or other metal, exhibiting the usual crystalline granular

[1] *Proc. Roy. Soc.*, vol. 65, p. 85.

FIG. 34. Ferro-tungsten, with 28°/₀ tungsten. ×200 dia.

FIG. 35. Ferro-chrome, with 20°/₀ chromium. ×200 dia.

FIG. 36. Ferro-nickel, with 52°/₀ nickel. ×200 dia.

UCSF

FIG. 37. Cleavage fracture through grains. Distorted and fractured after polishing, showing sliding just starting. ×130 dia.

structure, was stretched beyond its elastic limit a remarkable change occurred in the polished and etched surface. A number of sharp black lines appeared on the surfaces of the grains, parallel to each other in each grain, but in different directions in different grains.

The appearance of each grain is so like a crevassed glacier that these dark lines might be readily taken for cracks. Against this, however, is the consideration that an overstrained piece of iron recovers its original elasticity after a period of rest, but the dark lines do not disappear, and further, that sharp lines of the same nature are not seen on the surface of metal which has been polished and etched after straining. The lines are not therefore cracks, but slips along planes of cleavage or gliding planes. These are termed slip bands. When a metal is much strained a second system of bands appears on some of the grains crossing the first system at an angle, and in some cases showing little steps where the lines cross. These bands are due to slips occurring in a second set of cleavage or gliding planes. By these changes a dull appearance is produced on the originally bright surface. Straining of a polished surface of metal appears to produce the same effect as that of etching, and causes the boundaries of the grains to be revealed. Fig. 37 is from a photograph by Mr. Stead.

Slip bands are developed by compression as well as by extension, and exhibit all the characteristics which they present in stretched pieces, so that no difference can be discerned between the effects produced in both methods. By twisting an iron bar well beyond the elastic limit the slip bands are made to appear, for the most part, in directions parallel and perpendicular to the axis of twist. A strip of sheet copper or iron, when bent and unbent in the fingers, shows them well developed by the extension and compression of the surface. A beautiful development of slip bands may readily be produced by pinching a button of polished silver or copper in a vice.

In fine-grained steel the slip bands can only be seen with very high powers in consequence of the minute size of the crystal grains.

The above-mentioned experiments throw a new light on the character of plastic strain in metals and other irregular crystalline aggregates. Plasticity is due to slip on the part of the crystals along cleavage or gliding surfaces. Each crystal grain is deformed by numerous internal slips occurring at intervals throughout its mass. In general these slips occur in three planes, and the combination of the three allows the grain to accommodate itself to its envelope of neighbouring grains as the strain proceeds. The action is not a homogeneous shear, but a series of finite slips, the portion of the crystal between one slip and the next behaving like a rigid solid. The authors infer from their experiments that "flow," or non-elastic deformation in metals, occurs, through slips between portions of each crystalline grain on one another, along surfaces of cleavage. The portions which slip are considered to be perfectly elastic. The slip, when it occurs, involves the expenditure of work in an irreversible manner. It is because the metal is an aggregate of irregular crystals that it is plastic as a whole, and is able to be deformed in any manner as a result of the slips. The surfaces over which the slip occurs are at first weak, but heal with the lapse of time.

Slip bands probably occur in all metals, and are in themselves an evidence of crystalline structure, for the elementary pieces which slip over each other retain their crystalline character. The experiments on strain have also been extended to eutectic alloys. These alloys exhibit rather large grains, which consist of an intimate mixture of two constituents. Straining has the effect of making this intimate mixture more apparent by causing slips, which set up differences of level between the particles of the two constituents. The study of the

micro-structure of alloys suggests an explanation of the cause of variation of electrical conductivity with temperature. The components of an alloy, having different co-efficients of expansion, will depend on temperature for the closeness of the joints. Thus, if the more expansible metal exists as plates, the effect of heating will be to make the joints between the two conduct more readily, but the well-known resistance of alloys generally is probably due to the larger number of joints across which the current has to pass.[1]

[1] Bakerian Lecture, *Proc. Roy. Soc.*, p. 172, vol. 65.

# CHAPTER VIII.

## COPPER.

§ 59. COPPER has been known from the earliest times, and its valuable properties justly esteemed in all ages. It forms with other metals a series of alloys far more numerous and important than that of any other metal, which may be accounted for by its red colour, high malleability, ductility, toughness, softness, and tenacity, which properties it imparts in a great measure to many of its alloys, even when united with metals opposite to it in character, such as zinc. Next to iron it may be considered the most useful of all the metals both from its valuable properties when used alone, and its intrinsic value as a constituent of alloys. The very properties which make copper so useful are sometimes a disadvantage for certain purposes; for instance, the toughness and closeness of grain make it more difficult to turn in a lathe than brass; and its softness makes it unfit to be used alone for objects subjected to great wear and tear. In the vast majority of cases in which copper is used it has to be melted and cast into moulds of various kinds, in order to prepare it for further treatment, and the difficulties in producing sound castings are so great, that it can only be successfully manipulated in the hands of a very skilful and experienced workman; even then a

common practice is to add some other substance, so that it is probably not too much to say that pure copper has never been cast in considerable quantity, so as to produce a good ductile casting free from blow-holes. Great attention has been directed to this subject of late years in consequence of the demand for solid-drawn copper tubes, rollers, etc.; and different physics have been added to the copper in melting, with a view of overcoming the inherent defects.

It must be borne in mind that pure copper is not a commercial article, and although copper is now manufactured on a large scale in a purer state than previously, the metal retains ingredients which modify the valuable properties the metal possesses in its chemically pure state. The common impurities are iron, arsenic, antimony, bismuth, and sometimes sulphur, tin, lead, nickel, cobalt, and gold. These elements even in very small quantities seriously affect copper, but they may be neutralised to some extent by uniting them with oxygen. When such metal is melted in contact with air, some of the copper is oxidised, forming cuprous oxide, $Cu_2O$, which makes the whole mass brittle and unworkable; it is termed "underpoled" copper. Some air or carbonic oxide is also retained in the gaseous state, and on the metal solidifying at the surface some of this gas will be enclosed in the interior of the mass, and produce a honeycombed structure. To prevent access of air, the metals may be covered with charcoal, and this when used judiciously may be effective, but the great difficulty is to know when the carbon has done its work. Carbon in contact with air will produce carbonic oxide, and this gas probably penetrates the copper to some extent and removes the oxygen; but if any further excess of carbonic oxide is admitted, it may reduce the oxides present as impurities, as well as oxide of copper, and the elements being liberated, will alloy with the copper, making it brittle and analogous in properties to what is technically

known as "overpoled" copper. Seeing, then, that commercial copper is impure, but that the impurities may be neutralised to a great extent by oxygen, the problem is to discover the point when this end has been attained, without introducing an excess of air. On the other hand, it may be as efficacious, and much more easy, to admit an excess of oxygen, and subsequently remove it, by adding some body which has a stronger affinity for oxygen than copper has.

The tenacity of copper in the cast state is about 8 tons per square inch, but this is considerably increased after the metal has been worked, especially when drawn into wire. It may be obtained in the pure state by the electrolysis of its pure salts, such as the sulphate and chloride. It is one of the best conductors of electricity, and this forms a good means of judging of its purity.

The varieties of commercial copper are:—rosette or Japan copper, the surface of which presents a peculiar red colour, due to a coating of oxide, formed by throwing water on the surface of the metal while in a heated state. Bean-shot and feathered-shot copper, which are obtained in the form of globules and flakes respectively, by running the metal into hot or cold water. Tough-cake is a variety cast into rectangular slabs, convenient for rolling, etc. Best-selected is the name applied to the purest variety of commercial copper, special care being taken to free it from sulphur, arsenic, antimony, and iron. Russian-copper, which generally contains traces of iron, but is otherwise very pure. Chili-bars. This variety, as imported into this country, is prepared in bars weighing about 200 lbs. each; the copper being in a raw state, requires to be refined.

§ 60. The microscopic structure of copper varies with the mode in which it has been produced and also with its purity. A sample of electrolytic copper is confusedly crystalline, the surface appears to be a mass of crystals of various sizes with sharp angles piled one against the

FIG. 38. Electrolytic copper. ×200 dia.

FIG. 39. Pure cast copper. ×50 dia.

FIG. 40. Copper with 0·5% sulphur. ×50 dia.

other without any amorphous matter to cement the particles together. A section of electrolytic copper is depicted in fig. 38. When pure electrolytic copper has been melted and well stirred with a charred stick it presents a totally different appearance, being composed of polyhedral crystal grains, with rounded contours instead of sharp angles. In fact there is a great similarity in this respect with other pure metals, such as iron, gold, silver, etc.

Fig. 39 represents a sample of pure cast copper. Commercial copper is not pure, and therefore the presence of impurities tends to alter the structure, depending upon the quantity and the nature of the elements present. A small quantity of sulphur produces an effect illustrated in fig. 40. This section was polished and etched by prolonged immersion in hydrochloric acid. The effect of sulphur seems to be an intrusive one. It is as though the sulphur forms a fusible compound, which penetrates the otherwise larger crystals of copper, breaking them up into a number of smaller ones. The boundary lines are not continuous and regular, but vary in thickness as though the copper had broken through them in many places, or that the sulphide of copper, which is presumably present, had been unable to pursue a continuous course and had to jump over certain obstacles at intervals. In addition to this more or less round spots occur frequently in the meshwork.

Copper and oxygen have a strong affinity for each other at high temperatures, and when the copper is in excess the compound formed is cuprous oxide, $Cu_2O$. That copper is capable of dissolving certain proportions of this oxide is generally recognised, and that the presence of oxygen in copper causes contraction in a cast ingot is seen by the depression of the solidified surface, causing a longitudinal depression. If the oxygen existed in the gaseous state this would not be so, therefore one is forced to the conclusion that it is

dissolved when the copper is liquid, but separates out in cooling, and thus influences the structure. A section of this underpoled copper is shown in fig. 41. It arranges itself in granular shadowy meshes, not only around the primary crystals but in the interior of the latter, which probably accounts for the dulness of the colour and lustre as compared with pure copper, or with tough pitch copper. It is well known to be a source of weakness. In the case of commercial copper, containing small quantities of impurities, such as arsenic and antimony, whose influence will be afterwards discussed, the presence of a small quantity of cuprous oxide is necessary to neutralise the injurious effects of such elements, which are supposed to be rendered partially inert by oxidation, through the medium of the cuprous oxide. If, however, an insufficient quantity of oxygen be introduced for this purpose, the impurities exert their natural influence by forming alloys with a portion of the copper and causing an expansion of the mass, as seen by the longitudinal ridge on the surface of a cast ingot. The copper is then said to be overpoled. An illustration of a section of overpoled copper is seen in fig. 42. It produces a thick network of hard alloys in which the crystals of pure copper are embedded.

§ 61. **Phosphorus.**—A small quantity does not sensibly alter the colour of copper, but a large quantity renders it grey. One half per cent. makes it very hot-short, and only capable of being rolled in the cold, without cracking. A little phosphorus, say 0·1 per cent., added to molten copper in a crucible promotes soundness in the subsequent casting. Phosphorus increases the fusibility and hardness of copper, and when present in quantity, renders it brittle at the ordinary temperature. Copper containing 11 per cent. of phosphorus is extremely hard, of a steel-grey colour, is susceptible of a fine polish, but readily tarnishes. In making phos-

FIG. 41. Underpoled copper. ×50 dia.

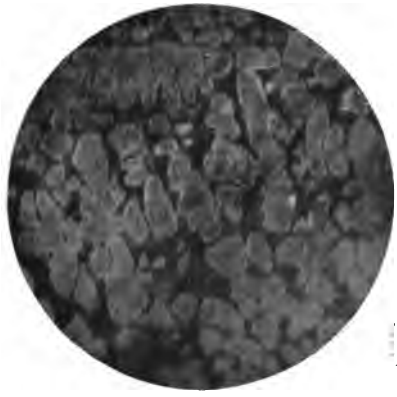
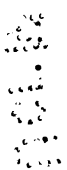


FIG. 42. Overpoled copper. ×50 dia.



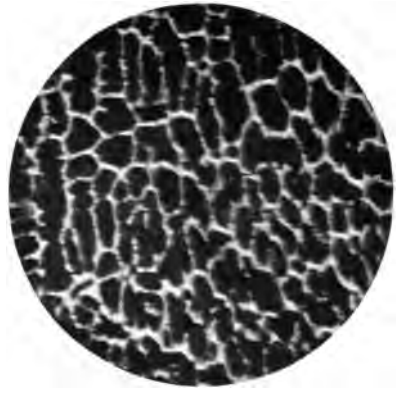


FIG. 43. Copper with 1°/₀ phosphorus. ×50 dia.

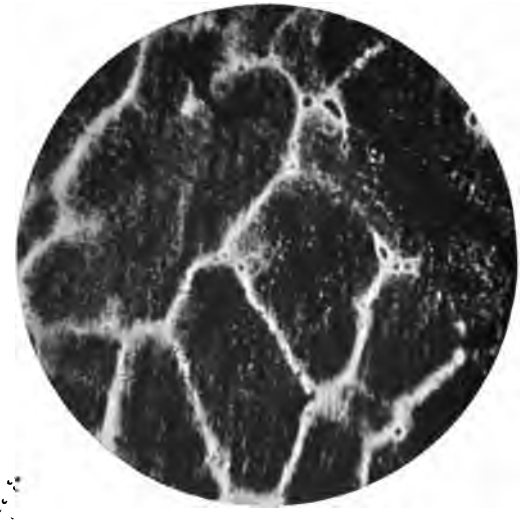


FIG. 44. Copper with 0·25°/₀ silicon. ×50 dia.

phorised copper, by adding phosphorus direct, the metal should not be stirred with an iron rod, as phosphorised iron will also be formed, and alloy with the copper. The effect of phosphorus on copper as regards the microscopic structure is seen in fig. 43. This is a section of electrolytic copper to which 1 per cent. of phosphorus has been added. A close resemblance to that of underpoled copper will be observed when viewed with low powers, but on examination with a high power the ground-mass is seen to consist of a granular eutectic mixture, probably of copper and a phosphide of copper, which covers a considerable portion of the surface. On etching the specimen in hydrochloric acid it also immediately turns a deep bronze colour, but under the microscope the boundary lines show up very brilliantly.

§ 62. **Silicon.**—Copper is contaminated with silicon when strongly heated in contact with sand and carbon. Copper containing 2 per cent. of silicon resembles gun-metal in colour; is tough, harder than copper, red-short, but may be rolled in the cold. Mr. Anderson, of Woolwich, found copper containing 1·82 per cent. of silicon tougher than gun-metal. If the temperature employed in heating the copper be too low, or not sufficiently prolonged, only a little silicon will be reduced, and the metal will resemble slightly underpoled copper. In a microscopic section the primary crystals of copper are fairly large, the silicon alloy appearing to be superimposed on the copper crystals as well as forming a network round them. They will be seen by reference to fig. 44 to form an elongated meshwork, existing apparently independently of the copper, yet this cannot be so, as the copper is closer in grain when seen in mass. Doubtless the silicon deoxidises the copper, if the oxygen is in excess, and tends to produce tough copper. The above section contains 0·25 per cent. of silicon.

§ 63. **Antimony** renders copper harder. Up to 0·5 per cent. it increases the strength and durability of copper, but when simultaneously present with other metals this advantage probably ceases. One per cent. and upwards imparts to the fractured surface a dull yellowish-grey colour. It is more injurious than arsenic. Fig. 45 shews copper containing 0·5 per cent. of antimony. It will be seen that antimony produces a meshwork round the crystals of copper with thick walls, out of all proportion to the quantity of antimony present, and that these walls are very irregular and discontinuous. Professor Arnold says that "with a high power the antimonide meshes are found to possess a distinctly compound structure, consisting of alternate dark and light laminae, suggesting that in the first instance an attenuated antimonide involves the copper crystals at a high temperature, but that at a low temperature the walls split up into plates of pure copper, alternating with those of a less basic antimonide. In this alloy the secondary crystals of copper contained within the antimonide membranes consist of remarkably perfect octahedra. Thick walls usually enclose very geometrical secondary crystals, suggesting that the perfection of the latter is due to the protective action of the walls in relieving the crystals themselves from contraction stresses."[1] When a section is etched with hydrochloric acid the figures are not so plainly revealed as with most other impurities occurring in copper, and requires a prolonged immersion to bring out the details.

§ 64. **Arsenic.**—Copper and arsenic readily combine when metallic arsenic is dropped into molten copper. When a very small quantity is thus added, the metal may be cast into a sound ingot, which contracts during solidification like phosphorised copper, and may be rolled cold, and afterwards drawn into fine wire. One half

[1] *Engineering*, Feb. 7th, 1896.

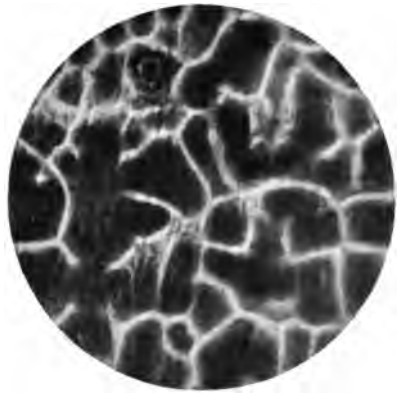


FIG. 45. Copper with 0·5% antimony. ×50 dia.

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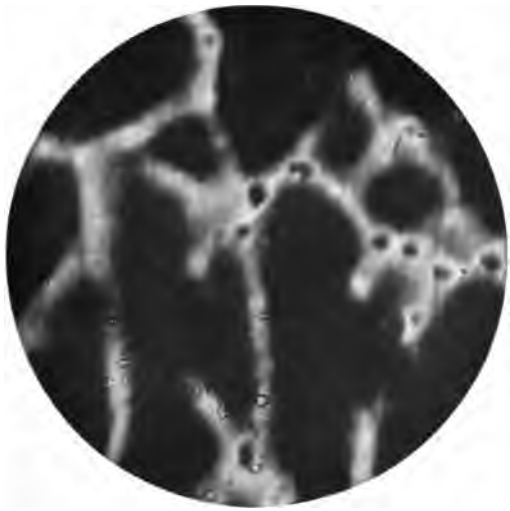

FIG. 46. Copper with 0·5% arsenic. ×200 dia.

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to 1·0 per cent. arsenic increases the tensile strength of commercial copper, but does not seem to materially alter that of pure copper. Quantities up to 0·5 per cent. greatly increase the durability of copper which has to be considerably heated, as in the case of the plates of fire-boxes of locomotives. Much arsenic is highly injurious, making the metal hard and brittle. Arsenic readily combines with copper when one of its compounds is heated with charcoal in contact with copper.

It is not easy to understand why arsenic is less injurious to commercial copper than antimony, seeing that the microscopic structure is similar, but it is very noticeable that the structure is much more readily revealed with arsenic than with antimony, and the boundary meshwork has somewhat thinner and more continuous walls. A representation of copper containing 0·5 per cent. of arsenic is given in fig. 46. There is reason to believe that with perfectly pure copper the influence of antimony is about the same as that of arsenic, but with impure copper antimony is much more injurious. Now, arsenic is always present in commercial copper and antimony is not, and it may be that the simultaneous presence of both elements is the cause of the disturbance.

§ 65. **Bismuth.**—This metal exerts a specially injurious influence on copper, a very small quantity makes it hot-short and cold-short. 0·1 per cent. makes copper so weak that at gradually rising temperatures the fall in tenacity is very rapid. Even ·002 per cent. considerably reduces the elongation. The explanation given for this deleterious action by Roberts-Austen is that, however poor or rich in bismuth the copper may be, a portion of bismuth, with perhaps a little copper, remains fluid until the temperature of the mass has fallen to 268° C., which is the melting point of bismuth. The microscopic structure of copper containing 0·5 per cent. of bismuth

is shewn in fig. 47, in which a striking peculiarity is observed in the cell walls, which instead of being single as in the previous cases, are double, with a dividing line down the centre. These walls are probably composed of the very fusible eutectic before referred to, and will therefore fully explain the extremely injurious effect produced by bismuth on the strength of copper. This fusible alloy does not confine itself to the cell wall but also penetrates the pure copper and segregates in patches. Professor Arnold found that during the polishing of copper containing bismuth, isolated globules of the fusible bismuth alloy, and portions of the membranes themselves, fell out, the result being that the polishing track on the kidskin became coated with a grey powder, and an increase of the friction was manually distinct. This peculiar structure will explain the enormous falling off of electric conductivity when a little bismuth is present in copper. See also fig. 18.

§ 66. **Zinc** in very small quantity does not much alter the character of copper, except to make it harder, but when over 0·6 per cent. is present it becomes hot-short. Fig. 48 shows the microscopic structure of copper with 0·5 per cent. of zinc. The crystal grains are much smaller and the walls thicker than in the case of pure copper, but with this exception there appears nothing particularly noticeable in the structure.

§ 67. **Aluminium** in copper up to 0·5 per cent., even under a low power, shows a large polygonal structure, fairly continuous, and with thick walls, which are brighter and more luminous than the interior. In some parts of the section the polygons are marked out by very fine lines. Aluminium has a powerful deoxidising effect on copper, hence the soundness and closeness of grain, and this is still more intensified by its solvent power for other gases likely to be present. Fig. 49 shews a sample of copper containing 0·5 per cent. of aluminium.

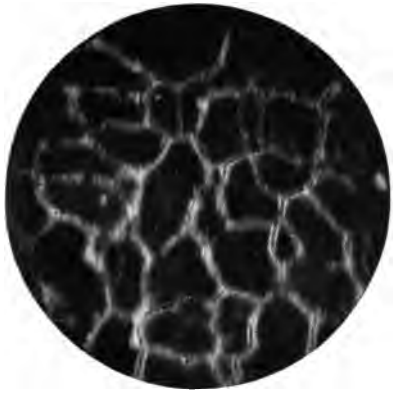

FIG. 47. Copper with 0·5% bismuth. ×50 dia.

FIG. 48. Copper with 0·5% zinc. ×50 dia.

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FIG. 49. Copper with 0·5% aluminium. ×50 dia.

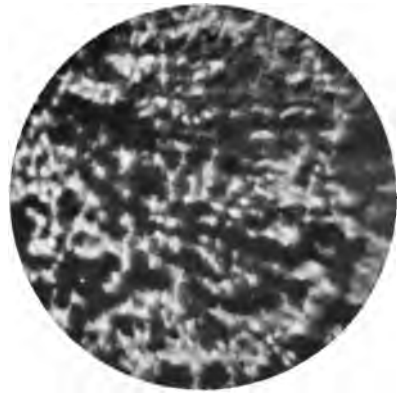

FIG. 50. Copper with 1% manganese. ×50 dia.

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§ 68. **Manganese** unites with copper in various proportions producing close-grained alloys, which may be tenacious, hard, and more or less ductile according to the amount of manganese present. It has a strong affinity for oxygen, and therefore acts as a powerful deoxidiser. Manganese in copper greatly increases its electrical resistance. Fig. 50 shews a section of a sample of cast copper containing about 1 per cent. of manganese. It differs in many respects from the other elements previously described with regard to its effect on copper. The crystal grains are more angular, and there is an absence of the mosaic structure so common in impure copper. It reminds one forcibly of the effect of manganese on iron with its large crystalline plates, some of which present their faces and others their edges. The substance of the crystal grains is a white homogeneous ground-mass, which is largely occupied by dark granular matter of a similar appearance to that of the boundary meshes. The latter are fairly thin and very discontinuous, as though the granular matter had burst through them. In some parts the mesh is double, probably due to cleavage along the joints. From the foregoing description it is easy to conceive how the conductivity is influenced by the structure. There is little doubt that recrystallisation occurs during the cooling from a high temperature.

# CHAPTER IX.

## BRONZE.

§ 69. **Bronze.**—This word will be used for the most part in this work to signify alloys consisting chiefly of copper and tin. Ancient bronzes differ considerably in the proportions of their constituents, but in the main copper and tin only were used. Sometimes other ingredients were added, either purposely to produce a given effect, and it may be some of these were present as impurities. Of late years very great attention has been given to the study of copper-tin alloys, and those proportions of the constituents which have been found by experience to give the greatest strength and the keenest cutting edge are the same as those used by the Greeks and Romans for their weapons of the chase and of war. The effect is produced by causing the bronze to undergo a process of hammering, as well as a method of hardening by heating and slow cooling. In addition to copper and tin, certain varieties of bronze containing zinc, lead, manganese, iron, silicon, or phosphorus, are now largely manufactured for machine and engineering purposes. Of these, alloys consisting of copper, tin, zinc, and lead are the most common, and are termed gun-metal.

Zinc in small quantity added to copper and tin has often a beneficial effect, as in casting, for instance, the

metal runs thinner, fills up the moulds, and is freer from blowholes. If the zinc exceeds what is required for this purpose the alloy is weaker but harder. The amount of zinc should not exceed 2 per cent. when high tenacity and elasticity are desired A small proportion of lead makes the alloy more workable and perhaps denser. If too much is present the lead will separate out on cooling. Iron hardens bronze and increases its resistance to wear in cases where it is subjected to much friction.

Phosphorus increases the physical properties of bronze in some respects. It has a refining influence on the mixed metals by uniting with any oxygen that may be present. It promotes soundness in the casting. If more than a small quantity is present it will unite with the alloy and harden it at the expense of the toughness, but the alloy still possesses considerable tenacity, and is very useful for certain purposes. Phosphor-copper, containing about 10 per cent. of phosphorus, is used in the preparation of phosphor-bronze. It is extremely hard, steel grey, and easily fusible. Phosphor-tin is a highly crystalline, brittle, and fusible body, generally made to contain about 10 per cent. of phosphorus. It is used in the manufacture of phosphor-bronze.

Very small quantities of sulphur, arsenic, and antimony render bronze brittle. The physical properties of bronze depend upon the composition, mode of manufacture, mechanical treatment, and rate of cooling after heating. The alloys having the chemical formulae $SnCu_3$ and $SnCu_4$ are the only ones which remain constant on re-melting, and their melting points lie between 600° and 700° C. With other proportions liquation occurs. The greatest density is found in the alloy $SnCu_3$. The hardness, reckoning from pure tin, increases with the proportion of copper up to 35 per cent., and this with more cupriferous alloys up to 73 per cent. are extremely brittle. Beyond this the hardness diminishes as the copper increases. The alloy $SnCu_3$ is distinguished

from the rest by several characters; it is homogeneous after repeated fusion, is peculiar in colour, has the highest density, exhibits the greatest degree of contraction, and is so brittle that it may be pounded in a mortar.

According to the amount of tin present in bronze the colour varies between red and white, and with a large excess of tin it becomes steel-grey. Tin whitens copper more than zinc. With 89 per cent. of copper and upwards the alloys are reddish-yellow or red. The 88 per cent. alloy is orange-yellow, the 85 per cent. alloy is pure yellow, and with 72 per cent. of copper the alloy is white. The greatest strength is found in gun-metal, with 90 per cent. copper and 10 of tin. From practical experience it has been found that the greatest strength is obtained by so working as to make the crystals of the alloy as small as possible, even the kind of mould in which the casting is effected exerting an influence upon the grain and through this upon the strength.[1]

The alloys of copper and tin have been carefully investigated by different workers in various ways, including microscopic examination. Behrens states that "alloys with from 2 to 6 per cent. of tin produce a network of yellowish threads in a reddish metal. Bronzes with 8 to 15 per cent. of tin show cruciform and dendritic groups of cubic crystals from orange to dark yellow, in a homogeneous matrix of a lighter yellow. With 15 to 20 per cent. of tin the matrix is nearly white, the crystals light yellow, very small, and arranged on lines that cross each other at right angles. The matrix is harder than the crystals; when white, the hardness rises above 4 (copper = 3); at the same time it shows more resistance to solvents. Caustic ammonia is a very good solvent for etching bronze. It chiefly dissolves the copper; at a more advanced stage of the etching, however, tin is also dissolved as stannous oxide,

[1] *Mixed Metals.* Macmillan & Co., 1901.

probably by a secondary action of the ammoniacal solution of cupric oxide."[1]

Professor Roberts-Austen and Dr. Stansfield have shown that disengagements of heat take place at different temperatures on cooling copper-tin alloys, and therefore that solidification occurs at different times. Thus, with 75 per cent. of copper the commencing solidification is probably due to the crystallisation of pure copper; at 770° C. there is a second disengagement of heat, corresponding to the freezing of the first eutectic, and lower still a third disengagement of heat between 500° and 600° C. In alloys rich in tin there is an evolution of heat at 227° C.

§ 70. Mr. Stead says[2] "on polishing slowly cooled alloys and etching with very dilute nitric acid it is possible to detect, even in an alloy with 0·1 per cent. of copper, fine bright needles; and these increase in size, both in length and diameter, with each addition of copper. In the alloy in which the proportion of copper amounts to 2 per cent. the crystals were completely separated by long digestion in dilute nitric acid (1 to 10), followed by treatment with dilute hydrochloric acid, which readily dissolves the hydrated metastannic acid formed by the nitric acid. The crystals so obtained were well formed, the edges perfectly angular, and the sides bright, smooth, and metallic. In form they were apparently square prisms, and occasionally several of them were found together forming a more or less plate-like structure. With 3 to 5 per cent. of copper the tendency to grow into plates was greater. With 10 per cent. of copper the separated crystals were badly formed and were nearly all in the form of plates with most irregular, granulated, uneven surfaces, but occasionally well formed needle-shaped crystals protruded from the

[1] *Microchemical Analysis*. Macmillan & Co., p. 205.
[2] *Jour. Soc. Chem. Indus.*, p. 506, 1897.

ends of the plates. From this alloy up to the composition SnCu containing 34·7 per cent. of copper, all the separated compounds were similar in appearance, and excepting at the ends of some of the plates there were no clearly defined crystalline forms present."

All the crops of crystals were analysed with the following results:

| Alloy. | Crystals Separated. | |
|---|---|---|
| | Copper. | Tin. |
| 98 per cent. tin and 2 per cent. copper, | 34·58 | 65·42 SnCu |
| 97 ,, ,, 3 ,, ,, | 36·50 | 63·50 |
| 95 ,, ,, 5 ,, ,, | 39·80 | 60·20 |
| 90 ,, ,, 10 ,, ,, | 44·60 | 55·40 $Sn_2Cu_3$ |
| 85 ,, ,, 15 ,, ,, | 47·20 | 52·80 |
| 80 ,, ,, 20 ,, ,, | 53·00 | 47·00 |
| 65·3 ,, ,, 34·7 ,, ,, | 56·12 | 43·88 $SnCu_3$ |

Now, from similar alloys, Mons. H. Le Chatelier and Mr. Laurie obtained crystals quite pure, having the exact formula $SnCu_3$, but Mr. Stead failed to obtain this compound by his method, as shown in the above analyses. In his trials a large quantity of an alloy of the composition SnCu was made, and the soluble eutectic was then dissolved and the separated compounds analysed. "This proved to have the composition approximating to $SnCu_2$. The micro-structure showed the presence of the edges of thick, bright plates, and a compound readily dissolved away, which left a darkened etched surface of practically pure tin. It is evident that such a compound as SnCu could not be melted by itself without undergoing change, and is another instance of the same thing that occurs when carbide of iron, antimonide, arsenide, or phosphide of tin are melted by themselves."

"It is possible that all the various separate com-

Not to be taken away

FIG. 51. Bronze with 20°/₀ tin. ×200 dia.

FIG. 52. Bronze with 83°/₀ tin. ×50 dia.

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FIG. 53. Bronze with 75°/₀ tin. ×50 dia.

FIG. 54. Gun metal with 10°/₀ tin. ×200 dia.

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pounds, containing more copper than sufficient to make SnCu, may be mixtures of molecules of that composition, with other molecules containing a larger atomic proportion of copper. The fact that needle-shaped crystals were found at the ends of some of the plates, and that certain retardations in cooling were observed by Professor Roberts-Austen, rather strengthens the view that they may contain more than one chemical compound." The fusible eutectic is very readily seen when the proportion of tin is 60 per cent. and the copper 40 per cent.

§ 71. M. Charpy states that with alloys containing from 0 to 25 per cent. of tin it is easy to prove the separation into two parts, the one coloured reddish-yellow and the other nearly white. Polishing alone suffices to separate these two substances in alloys containing 18 to 25 per cent. of tin. In metals rich in copper it is preferable to slightly etch with hydrochloric acid, and to lightly repolish afterwards; the light parts are then clearly seen, with clearer contours as the alloy is richer in tin. These white bodies surround dendrites strongly coloured yellow, which is probably the first eutectic alloy with 27 per cent. of copper. Fig. 51 shows a bronze with 20 per cent. of tin. The well-known striated appearance of the eutectic alloy is evident.

In alloys with 10 to 33 per cent. of copper, simple polishing suffices to reveal very hard needle-shaped crystals embedded in a fine groundwork. Fig. 52 contains 17 per cent. of copper. These crystals have a tendency to form irregularly-shaped bodies when the metal is allowed to cool very slowly, as seen in fig. 53. Alloys with 55 to 65 per cent. of copper have a nearly homogeneous structure, but when the proportion reaches 70 per cent. hard crystalline grains appear, surrounded by another substance, slightly more coloured, and much more rapidly oxidised by heating in air. This is probably the eutectic alloy with 73 per cent. of copper. It

appears, then, that with alloys containing less than 70 per cent. of copper the proportion of the eutectic alloy is too small to admit that the metal is formed of dendrites of copper embedded in an eutectic alloy. If the metal is rapidly cooled the eutectic may disappear, even in alloys with less than 7 per cent. of tin, while it is clearly developed in a 2 per cent. tin alloy cooled slowly.

With alloys containing more than 73 per cent. of copper, dendrites of copper are embedded in an eutectic alloy. Fig. 54 shews the structure of gun-metal containing 90 per cent. copper, and a sample of bell-metal containing 80 per cent. of copper, as shewn in fig. 50, exhibits the same structure more highly magnified.

§ 72. Prof. Campbell[1] has made an elaborate investigation of the alloys of copper and tin, and, as a result of his microscopical experiments, concludes that: When one per cent. of copper is present the first eutectic alloy is obtained, and between pure tin on the one hand and this alloy containing one per cent. of copper on the other, tin is found crystallising first in grains, then in dendrites in the eutectic. When the amount of copper exceeds one per cent., thin bright needles are seen, which increase in size and number until 8 per cent. of copper is reached. A third constituent is seen when the copper exceeds 8 per cent. We have the eutectic, or ground-mass, enclosing the bright porphyritic crystals, but these bright crystals are seen in places to have grown on and around a different kind of crystal, which is easily distinguished from the rest, because it turns black on lengthened exposure to the air, and a sharp line of junction can be seen between the two constituents. With a further increase in copper, the more easily oxidised crystals increase in size and number, while the bright crystals and the eutectic begin to

[1] *Engineering*, p. 28, Jan. 3rd, 1902.

diminish. So that with more than 8 per cent. of copper these readily oxidised crystals are the first to crystallise, then the bright crystals, and lastly the eutectic solidifies.

When the amount of copper reaches 41 per cent. another change has occurred, the mass contains small lath-like rods surrounded by a bright constituent. As the copper increases, the eutectic diminishes, and at 56 per cent. disappears. The readily oxidisable constituent steadily increases up to 61·7 per cent. of copper when the whole mass is uniform and is the alloy $SnCu_3$.

From 61·7 to 68·28 per cent. of copper the higher compound $SnCu_4$ crystallises out, and at 68·28 per cent. the alloy is uniform. It is harder, of lighter colour, and more readily attacked by acids than $SnCu_3$. It is very brittle and takes a high polish. $SnCu_3$, on the other hand, has a marked cleavage.

From 68·28 to 74 per cent. of copper, where the second eutectic occurs, the alloys consist of the bright $SnCu_4$, surrounded by an eutectic. When the copper is increased above 75 per cent. the colour changes from bluish white to yellow, and a new constituent, consisting of yellow rounded grains, appears. This crystallises out first, and then a bright white substance forms round it and in the eutectic. With a further increase of copper, the yellow grains increase, forming dendritic skeletons, and altering from yellow to red as pure copper approaches. This change of colour is due to the fact that the dendritic copper contains some tin in solution which makes it yellow or reddish according to the amount present. Between 90 and 95 per cent. of copper, the eutectic gradually disappears.

§ 73. Special bronzes are now in general use, containing elements other than copper and tin. Silicon bronze contains 1 to 2 per cent. of silicon, about 10 per cent. of tin, and the rest copper. It forms an alloy of consider-

able strength and tenacity. The general structure is seen in fig. 55, magnified about 30 diameters and viewed by oblique light. The photograph was taken from metal as cast, without polishing or etching. The same alloy is shewn in fig. 56, viewed by direct light, after polishing and etching in dilute nitric acid, and magnified 200 diameters. The crystal grains are well developed, and the close, regular, interlocking structure indicates great strength and tenacity.

§74. Fig. 57 shews a similar alloy to the last with regard to copper and tin, but contains 0·5 per cent. phosphorus instead of silicon. The general structure is dendritic, but the boundary lines are much interrupted, and patches of a fusible phosphide appear to have segregated, which should produce brittleness. In the portions not containing these patches the structure indicates considerable strength.

§75. Fig. 58 shews a sample of bronze containing 10 per cent. of tin, 0·5 per cent. of arsenic, and the rest copper. The section indicates a similar alloy to that of phosphor bronze, and should possess similar properties.

§ 76. Fig. 59 shews an alloy of copper with 10 per cent. tin and 3 per cent. of rich ferro-manganese, and termed manganese bronze. The dendrites are large and of complex composition, containing the tin alloyed with copper. The dark ground-mass is also complex, and probably contains the iron and manganese with copper. The structure suggests a strong and hard alloy. The dark portion shews a striated appearance.

§ 77. Fig. 60 shews an alloy of 95 parts copper and 5 parts aluminium. The structure differs entirely from the preceding bronzes, and is only imperfectly revealed in the photograph. The white portions are a rich aluminium alloy, and in parts of this structure a still whiter aluminium compound has separated out. The

FIG. 55. Gun metal with 1·5% silicon, viewed by oblique light, without polishing or etching. ×30 dia.

FIG. 56. Same alloy as Fig. 55, but polished and etched in dilute nitric acid. ×200 dia.

FIG. 57. Gun metal with 0·5% phosphorus. ×50 dia.

FIG. 58. Gun metal with 0·5% arsenic. ×50 dia.

FIG. 59. Gun metal with 3% rich ferro-manganese. ×50 dia.

FIG. 60. Aluminium bronze with 5% aluminium. ×50 dia.

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FIG. 61. Aluminium bronze with 10% aluminium. ×50 dia.

FIG. 62. Brass with 66·6% copper. ×50 dia.

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# CHAPTER X.

## BRASS.

§ 78. This term is used to signify all alloys of copper and zinc, and as these two metals unite in various proportions a great variety of copper zinc alloys may be made, but only within certain limits are they of any great industrial importance, being generally limited to those that have a decidedly yellow colour.

Commercial brass never consists entirely of copper and zinc, since whatever impurities exist in the separate metals will also be found in the alloy, though probably in smaller quantity, the most common of these being lead, tin, iron, and arsenic. It often happens that some of these are purposely added to produce a given effect in the alloys. The colour of brass shows great variations, according to the proportions of the constituents, ranging from the red of copper at one end to the bluish-white of zinc at the other. But the change from red to white is not so uniform as a casual observer might suppose. Thus alloys containing 94 to 99 per cent. copper are red, with only a faint yellow tint; with 87 to 93 per cent. copper, the colour is reddish-yellow; from 79 to 86 per cent. copper, a yellowish-red tint prevails; below this, down to 74 per cent. copper, the alloys are yellow, with a content of 67½ per cent. copper, a reddish-yellow tint

is obtained; with 60 to 66 per cent. copper the colour is a full yellow; with 59 per cent. copper a reddish colour is obtained; with 52 per cent. copper the colour is nearly golden-yellow; with a less quantity of copper than the above, the colour of the zinc begins to overpower the red colour of the copper, the alloys becoming more lead-like in appearance as the proportion of zinc increases. Brass may be made pliable and soft, hard or brittle, strong or weak, elastic or non-elastic, having a dead surface or one highly polished, by varying the composition.

Copper and zinc may be united in all proportions, forming homogeneous alloys; and the combination is usually attended with evolution of heat. Certain varieties of brass are exceedingly malleable and ductile, and these properties, combined with the variety of shades of colour obtained by suitable mixing, and the moderate cost, render copper-zinc alloys most valuable for ornamental purposes. Brass possesses all the necessary advantages as a constructive material for works of art, and with the aid of transparent varnishes, termed lacquers, which have been brought to great perfection, it resists the action of the atmosphere remarkably well. The malleability of brass varies with the composition, with the temperature, and with the presence of foreign metals. Some varieties are only malleable when rolled cold, others can be rolled at any temperature. Alloys containing 1 to 35 per cent. of zinc can be drawn into wire, but those containing 15 to 30 per cent. are the most ductile.

Brass is harder than copper, and therefore better adapted to resist wear and tear. It acts well under the influence of a percussive force, as in the process of stamping, provided it is suitably annealed at proper intervals, in order to counteract the effects of local hardening, due to the compression of the particles into what may be termed unnatural positions. During the ordinary process of annealing the metal becomes coated

with a scale of oxide, by union with the oxygen of the air, which oxide requires to be removed at each stage. This is done by dipping the metal in aquafortis, or dilute sulphuric acid, then scouring with sand if necessary, and finally well rinsing in water. A piece of brass submitted to permanent deformation by mechanical treatment is more or less hardened, and its limit of elasticity is raised. With the same brass the author has obtained tensile strengths varying from fifteen to twenty tons per square inch before and after annealing. As will be afterwards pointed out, the temperature for annealing is of the greatest importance, for if the temperature is too low the reheating is inoperative, and if too high the metal is spoilt.

The mechanical properties of brass have been extensively studied by Charpy.[1] He took hard brass, produced by hammering and rolling cold, and tested its tensile strength before and after annealing at different temperatures. The test pieces were about 0·2 inches square, and 3·5 inches long between the shoulders. For compression tests he used cylinders 0·52 inches high and 0·32 inches diameter. For fragility he employed a weight of 22·5 lbs. falling through a distance of 40, 80, and 120 inches, etc., till the bar was broken or bent to an angle of 90°. The bars tested were 0·54 in. × 0·35 in. × 2·4 in. long. For all the alloys studied it was found that as a hard alloy was heated at gradually increasing temperatures the tenacity diminished, the elongation increased, and the section of the ruptured part became less, except at temperatures approaching the fusing point. From the ordinary temperature up to a certain point the effect of re-heating is nil. The temperature at which annealing begins to be effective depends on the amount of compression the metal has undergone. With regard to brass with upwards of 40 per cent. of zinc, the temperature for annealing must

[1] *Soc. d'Encour. pour l'Industrie Nationale*, 1886.

be lower, as the quantity of zinc is increased, for the same treatment increases the hardness, as the zinc is greater. When the limit at which annealing begins to be effective is passed, then the softening effect is increased with each degree of temperature raised, as shown by the greater amount of elongation, till finally a point is reached at which the annealing effect is at a maximum. The metal then has the maximum malleability and ductility. It is important to know this zone of complete reheating, since the lower the temperature required the quicker will the work be done, and the less will be the amount of fuel used. Take copper for example; if annealed at 420° C. it will be as soft and malleable as if heated at 900° C. For brass with 30 per cent. of zinc, the annealing temperature must be above 600° C. Beyond the zone of temperature within which annealing is most effective, the metal alters in structure and rapidly deteriorates as the temperature approaches that of the melting point. The metal is then said to be burnt. As a rule this burning zone will be higher the purer the metal. Brass containing lead and tin will be burnt at temperatures at which pure brass will be unaffected. A sample of brass with 70 per cent. copper, and containing 0·15 per cent. of tin and 0·2 per cent. lead, was burnt when heated above 800° C., while a similar alloy free from tin and lead was not sensibly burnt at 900° C.

The tenacity of brass gradually increases as the zinc increases from 0 to 35 per cent., then more rapidly up to about 40 per cent., when it is at a maximum, then it gradually decreases with more zinc. In a similar manner the elongation increases with an increase of zinc, and reaches a maximum at 30 per cent.

The mechanical properties of brass have also been made the subject of investigation by Professor Roberts-Austen.[1]

[1] Fourth Report Alloys Research Com. *Inst. Mechan. Eng.*, 1897.

He has shown that many of the brasses have more than one freezing point, and that the subsidiary freezing points represent euctectic alloys. These alloys were separated by squeezing away the fluid portions in a press, the temperature being accurately noted by means of a thermo-junction pyrometer. The maximum strength in cast brass is in the alloy with about 60 per cent. copper, and this has practically but one freezing point, although a feeble eutectic is revealed at 450° C. It is a well-known fact that the above composition, with a little iron added, has an increased tensile strength, but the cause was obscure. An alloy was made, consisting of 61 copper, 39 zinc, with 1½ per cent. of iron. This, upon being tested and a cooling curve obtained, showed that the low eutectic point was absent, and therefore the source of weakness had been removed. Moreover, the mean solidifying point was higher than that of the brass without the iron, which in itself is an indication of augmentation of strength. Where strength is required it would appear to be advisable whenever the presence of a low eutectic in an alloy is revealed, to add some third metal which will diminish the fusibility of the eutectic. The presence of an eutectic in an alloy also naturally diminishes the extensibility of any mass which contains more than a small amount of it.

The formation of copper-zinc alloys is generally attended with contraction, which attains its maximum in the alloy $CuZn_2$, containing 32·6 per cent. of copper. This alloy is brittle, and exhibits none of the characteristic properties of the constituent metals. The density of brass is increased by mechanical treatment, but this effect is annulled by sudden, and still more by slow cooling after annealing.

When an ingot of ordinary brass is broken while hot, its fracture is coarsely fibrous, but when broken while cold, it should be finely granular. When the fracture of a cast ingot of certain metals is fibrous, the directions

of the fibres will be at right angles to the cooling surface. In the case of a sphere, the fibres will have the direction of radii; and in the case of a square, two diagonals will be plainly visible on the transverse fracture, formed by the points of junction of the internal extremities of the fibres.[1] Mr. F. H. Storer[2] states "that the tendency to shoot into fibres extends from alloys containing 57 or 58 per cent. of copper down to those containing 43 to 44 per cent., where it gradually disappears. The tendency to form fibres is strongest in those alloys which contain nearly equal atomic proportions of copper and zinc, being less clearly marked as one recedes in either direction from this point, until a stringy texture, analogous to that of copper, is reached on one hand, and the peculiar pastiness of zinc on the other. In preparing crystals, this pastiness manifests itself decidedly in the alloys immediately below those which are fibrous, becoming more strongly marked as the alloys are richer in zinc. The fracture of these white alloys is for the most part vitreous or glassy."

Brass is occasionally obtained in crystals. Storer prepared the most perfect individual crystals from brasier's solder, which consists of equal parts by weight of copper and zinc, and occurs in the state of coarse powder, produced by heating the alloy to a sufficient degree and pounding it in a mortar while hot. The alloy containing 5 to 6 per cent. of zinc was found to crystallise remarkably well. It will be seen from the above remarks that the crystalline condition of copper-zinc alloys does not depend on an excess of zinc, as might be presupposed from the highly crystalline character of zinc. As before stated, zinc becomes malleable when worked at a temperature of from 100° to 150° C., but at higher temperatures it again becomes brittle. It

[1] Percy's *Metallurgy*, p. 608.
[2] *Mem. of Amer. Acad.*, 1860 (8), p. 35.

is assumed that the brittleness is intimately connected with the crystalline condition.

**Some Varieties of Modern Brass.**

| Name. | Colour. | Copper. | Zinc. | Tin. | Lead. | Iron. | Gold. |
|---|---|---|---|---|---|---|---|
| Jeweller's gilding alloy | Red - - | 94 | 6 | ... | ... | ... | ... |
| ,, ,, | ,, - - | 90·5 | 7·9 | ... | 1·6 | ... | ... |
| Pinchbeck - - | Reddish-yellow | 88·8 | 11·2 | ... | ... | ... | ... |
| ,, - - | Red - - | 93·6 | 6·4 | ... | ... | ... | ... |
| Orĕide (French gold) | Reddish-yellow | 90 | 10 | ... | ... | ... | ... |
| Talmi gold - - | Gold - - | 90·70 | 8·33 | ... | ... | ... | ·97 |
| Tissier's metal with one per cent. of arsenic | Red - - | 97 | 2 | ... | ... | ... | ... |
| Tournay's alloy - | Yellow - - | 82·54 | 17·46 | ... | ... | ... | ... |
| Rich sheet-brass - | ,, - - | 84 | 16 | ... | ... | ... | ... |
| Bath metal, similor, etc. | ,, - - | 80 | 20 | ... | ... | ... | ... |
| Dutch alloy - - | ,, - - | 76 | 24 | ... | ... | ... | ... |
| Bristol sheet-brass - | Bright yellow - | 72·8 | 27 | ... | ·2 | ... | ... |
| Brass wire - - | ,, - | 70 | 30 | ... | ... | ... | ... |
| Prince's metal - | Yellow - - | 75 | 25 | ... | ... | ... | ... |
| Sheet and wire brass | Full-yellow - | 67 | 33 | ... | ... | ... | ... |
| Mosaic gold, ordinary brass | ,, - | 66·6 | 33·3 | ... | ... | ... | ... |
| Bobierre's metal - | ,, - | 66 | 34 | ... | ... | ... | ... |
| Muntz' metal - | ,, - | 62 | 38 | ... | ... | ... | ... |
| ,, ,, - | ,, - | 60 | 40 | ... | ... | ... | ... |
| Gedge's metal - | ,, - | 60 | 38·5 | ... | ... | 1·5 | ... |
| Common brass - | ,, - | 64 | 36 | ... | ... | ... | ... |
| Aich's metal - - | ,, - | 60 | 38·2 | ... | ... | 1·8 | ... |
| French brass (Potin jaune) | Grey-yellow - | 71·9 | 24·9 | 1·2 | 2·0 | ... | ... |
| Hamilton's metal, Chrysorin | Full-yellow - | 64·5 | 32·5 | ·3 | 2·7 | ... | ... |
| French brass for fine castings | ,, - | 71 | 24 | 2 | 3 | ... | ... |
| Sterro metal - - | ... | 55·5 | 42 | ... | ... | 2·5 | ... |
| Hard solder for copper or iron | ... | 57 | 43 | ... | ... | ... | ... |
| Hard solder for brass | ... | 50 | 50 | ... | ... | ... | .. |
| Dipping brass - | ... | 53 | 47 | ... | ... | ... | ... |
| White brass - - | ... | 34 | 66 | ... | ... | ... | ... |
| Lap alloy - - | ... | 12·5 | 87·5 | ... | ... | ... | ... |

Charpy [1] states that brasses containing not more than 35 per cent. of zinc are entirely made up of a network of needle-shaped crystals. Above 35 per cent. of zinc the crystals do not fill the whole mass, but are embedded in glass-like magma. The crystals become fewer as the zinc is increased, until when the zinc reaches 67 per cent., a homogeneous structure with a conchoidal fracture is obtained. These facts explain certain known mechanical properties of such alloys. Thus in commercial brasses, containing less than 35 per cent. of zinc, small quantities of lead and tin form, as it were, a solder between the crystals, and weaken the alloys when they are raised above 200° C. When there is more than 40 per cent. of zinc the lead and tin are embedded in the glass-like magma, and do not weaken the structure; therefore, such alloys can be rolled hot. It is probable that alloys from 1 to 34·5 per cent. zinc are isomorphous mixtures of copper and $Cu_2Zn$; alloys with 35 to 67 per cent. zinc are mixtures of $Cu_2Zn$, a malleable substance, and of $CuZn_2$, a hard and brittle substance; alloys with more than 67 per cent. of zinc are mixtures of zinc and $CuZn_2$.

§ 79. Microscopic examination of copper-zinc alloys reveals the fact that different structures occur in the same alloy under different conditions of treatment, and that under normal conditions, in the cast state, the whole series of alloys may be divided into three distinct groups, based on the difference of structure in each of these categories. We may term the alloys containing 1 to 35 per cent. of zinc, group I.; those containing 36 to 45 per cent. of zinc, group II.; and those containing more than 45 per cent. of zinc, group III. The members of each of the first two groups have the same general structure and appearance.

Alloys with 1 to 35 per cent. of zinc are distinguished by dendritic crystals, formed of long rectilinear needles

[1] *Soc. d'Encour. pour l'Indus. Nationale*, 1896.

and united in groups, but too badly formed to admit of measuring the angles, although the network of crystals presents a large number of right angles. The size of these crystals varies with the rate of cooling, and generally the size is increased when the metal has been poured at a high temperature and allowed to cool slowly. Pouring at a lower temperature and quick cooling have the contrary effect. As the rate of cooling also modifies the mechanical properties, we may infer the properties from the relative size of the grain. For a given alloy the tenacity is greater as the grain is closer. When a metal is maintained at a high temperature, varying with the composition, the crystalline grains become more clearly defined and apparently larger. When a certain temperature is exceeded the dendritic structure is modified, the crystals are much larger, somewhat octagonal in shape, and with numerous well-defined angles. The temperature necessary to produce this change is, for alloys with 70 per cent. copper, from 750° to 800° C., and for alloys with 80 to 90 per cent. copper, 850° to 900° C.

Fig. 62 shows the nature of a section of cast brass containing 66 per cent. copper and 34 per cent. zinc. In order to compare this with samples of different qualities of copper sections of that metal are given in figs. 39-42.

§ 80. The methods of polishing sections of metals have already been described, and therefore need not be repeated here. Three methods of etching the members of group I. may be adopted, namely, by means of a solution of ammonia; by dilute hydrochloric acid; and by simply heating in air on a hot plate. The two former are preferable to the latter, and although the action is slow it is very effective. For metallic copper ammonia is used and may require two hours' immersion. A word of warning may save erroneous impressions being produced by secondary effects in the etching liquid. When brass

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FIG. 63. Stamped brass with 70% copper. ×200 dia.

FIG. 64. Stamped brass, strongly reheated, 70% copper. ×50 dia.

FIG. 65. Brass with 70% copper, after burning. ×50 dia.

FIG. 66. Stamped brass, burnt in annealing. ×50 dia.

is immersed in ammonia for instance, the copper dissolves more quickly than the zinc, producing a difference on the surface, which assists in revealing the structure. After a time the solution becomes light blue from the presence of dissolved copper and the latter begins to be deposited on the brass in the form of large crystals. On examining the section under the microscope we then get, not the true structure of the brass, but the structure of pure copper mixed with the structure of brass. The etching process should then be carefully watched and examined from time to time so as to stop the process when the action is complete and before the deposition of copper practically commences. Again, too vigorous etching in acids must be condemned, and mechanical imperfections, such as scratches, must be duly allowed for. If the section has been eaten into too much by the etching liquid the surface becomes too uneven to get all parts in focus at the same time, and is useless, except for general examination with a hand glass. In such a case it is advisable to rub it down again on the emery pad and repolish on the rouge block. Then etch again, taking care not to overdo it the second time. In no operation is it more important to observe the old adage "hasten slowly." Some experimenters use dilute nitric acid, and in the hands of an experienced worker it may be all right, but with a beginner it had better be avoided.

§ 81. When a member of group I. brass has been worked by drawing, hammering, or rolling, the structure is modified, the grain is closer, and a totally different appearance is observed. It is also less readily acted upon by etching liquids. The general effect is a more or less complete deformation of the crystals, with the production of a granular appearance. Fig. 63 shows the structure of worked brass containing 70 per cent. of copper, and fig. 64 shews a section of the same brass after being strongly

annealed. If samples are taken, of the same brass, after each passage through the rolls, polished, etched, and examined under the microscope, the appearance will approximately indicate the amount of pressure undergone. If such a metal be annealed at too low a temperature the structure is not sensibly modified, but if the temperature during the reheating is sufficiently high the crystal grains resume their former shape. At high temperatures the crystal grains preserve the same form but take a larger size and the shape is then more clearly developed. Charpy considers them to be octahedrons with numerous angles, the etching causes the crystals to stand out in relief and the orientation may be observed by rotating the section on the stage. In the photographs the clear parts correspond to clear faces and the dark parts to those in shadow.

§ 82. Fig. 65 shews a sample of brass with 70 per cent. copper, which has been so strongly reheated as to produce what is termed burnt brass, and the metal therefore spoiled so far as its working properties are concerned. The crystalline structure is now highly developed and small pit marks are seen, like bubbles of gas, becoming more numerous as the temperature is higher, and arranged round the crystals, forming an almost continuous network. This effect is probably due to impurities and is especially marked when notable quantities of easily fusible metals such as lead and tin are present. These metals form fusible eutectics and not only penetrate the spaces between the planes of the crystals, but also penetrate into the substance of the crystals themselves and corrode them. As these eutectic alloys have low melting points it is evident that they exercise a powerful influence on the properties of the metal. In proportion to the nature and amount of impurities present the temperature of annealing must be kept within certain limits, as a temperature which would

FIG. 67. Brass with 60°/₀ copper. ×50 dia.

FIG. 68. Brass with 60°/₀ copper, strongly annealed. ×50 dia.

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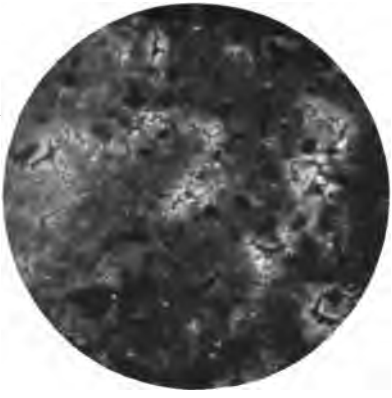

FIG. 69. Brass with 64·5°/₀ copper. ×50 dia.

FIG. 70. Brass with 54·5°/₀ copper. ×50 dia.

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entirely deteriorate an impure metal would have little effect on the properties of a pure metal. Fig. 66 shews a sample of commercial stamped brass which became so brittle on working after annealing as to crack badly and appeared to be completely spoiled. The microscopic structure revealed the cause, and showed it to have become quite crystalline with numerous dark segregations between the crystals, due to the presence of a fusible eutectic.

§ 83. The members of group II., containing 55 to 64 per cent. of copper, are distinguished from group I. by the curved form of the crystalline grains, which are more closely packed together, and present the appearance of an eutectic alloy. Charpy[1] considers it probable that they are formed of an isomorphous mixture of copper and of a compound having the formula $Cu_2Zn$. It is about the transition point between group I. and group II. that a variation of density and a modification of colour appear. The structure of a sample of brass containing 60 per cent. of copper is shown in fig. 67, and the same after strongly reheating in fig. 68. It will be seen that the effect of a strong annealing is to increase the size of the grain and the same applies to the metal when melted and allowed to cool slowly. By quick cooling the grain is finer but the shape is unaltered. One very significant feature of alloys of this category is that they are not altered in structure by being raised to the burning zone as is the case with alloys of group I. Etching very quickly brings out the structure. The liquid seems to dissolve an amorphous magma and leave in relief crystalline grains which appear to be malleable and break with difficulty by pressure, such as rolling. Rolling does not appear to alter the structure, except when the metal is rolled thin; the appearance then becomes granular.

[1] *Soc. d'Encour. pour l'Indus. Nationale*, 1896.

To alloys of this class, iron from 1 to 3 per cent. is sometimes added, as in delta metal, to increase the tensile strength. Now in an alloy of 61 per cent. of copper and 39 per cent. of zinc, Roberts-Austen found a low eutectic alloy at 452° C., and by adding 1·5 per cent. of iron this low eutectic was removed, the added iron entering into combination with the eutectic and forming with it a less fusible compound. Moreover the main solidifying point of the delta metal was found to be higher than that of the brass.

§ 84. Alloys of the second category with about 60 per cent. of copper probably consist of a solvent and an eutectic, the yellow, the portion least attacked by the acid, being that which separates first (the solvent) and the other the eutectic. When the alloy cools from a state of fusion, freezing commences at about 890° C., and is completed at 875°. At 890° C. the solvent compound of copper and zinc begins to freeze, and at a certain lower temperature the eutectic solidifies. As a result there is a solid mass in which the two alloys are alternated with each other in laminae.

It will be seen from the foregoing that the structure of brass varies with the composition, and while the members of the same category have a similar structure, they differ entirely from those of another category. It is therefore instructive to note the structure of those alloys which form the connecting links between the three types. Fig. 69 shows brass containing between 64 and 65 per cent. of copper, and contains both types of structure. The dendritic crystals with long rectilinear needles of group I. are intermixed with the curved interlacing crystal grains of group II. Fig. 70 is a sample of brass containing about 54 per cent. of copper, and shows the boundary lines of large crystal grains of group III., the interiors of which contain the fine interlacing structure of group II.

FIG. 71. Brass with 50°/₀ copper. ×50 dia.

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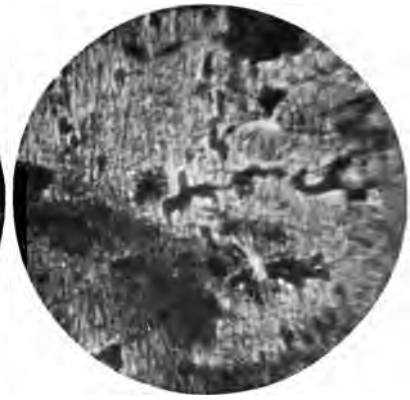

FIG. 72. Brass with 20°/₀ copper. ×50 dia.

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FIG. 73. German silver with 12°/₀ nickel. ×50 dia.

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FIG. 74. German silver with 12°/₀ nickel, after burning. ×50 dia.

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§ 85. The members of group III., containing less than 55 per cent. of copper are characterised by brittleness, and differ in structure from those of the preceding structures in the absence of the dominating needle-shaped and interlacing crystals, arranged more or less at right angles. The surface presents the aspect of an irregular patchwork consisting of different bodies, which assume different colours when acted upon by reagents. Charpy considers that solidification commences simultaneously round a great number of points and almost uniformly through the mass. Around each of these parts is a matrix, practically homogeneous. The prominent parts appear to have a hexagonal form, and are embedded in the matrix. When the crystallisation takes place in a large mass, gradually cooling in a mould, the solidification is less regular, and elongated crystalline grains are formed perpendicularly to the cooling surface. When the proportion of zinc reaches 50 per cent., smaller crystals are developed in the interior of the larger grains. Fig. 71 gives an idea of this kind of structure.

It has already been stated that alloys with 35 to 67 per cent. of zinc are probably mixtures of a malleable substance, having a composition corresponding to the formula $Cu_2Zn$, and of a definite chemical compound $CuZn_2$, which is hard and brittle, while alloys with more than 67 per cent. of zinc are mixtures of zinc and $CuZn_2$. The fact of the existence of the definite compound $CuZn_2$ has been placed beyond doubt by several different experimenters. It is therefore interesting to note the appearance of an alloy of copper and zinc in these proportions when a polished section is viewed under the microscope. It is seen to have a uniform structure like glass. When broken it has a conchoidal fracture. With more zinc than that required to form the compound $CuZn_2$, a polished section, etched with potash, shows small crystals, probably of zinc, embedded in

the compound $CuZn_2$. This structure is illustrated in fig. 72, which contains 20 per cent. of copper.

§ 86. The foregoing classification of different varieties of brass, according to the nature of the microscopic structure, will doubtless suffice to make manifest the importance of closely cultivating this means of investigation, which is capable of affording a satisfactory explanation of many of the defects constantly arising in industrial practice. It admits of showing in some degree the amount of work which has been put on a metal, whether it has been unduly strained in any particular process, and also whether the metal has been properly annealed or has been overheated and rendered less malleable and ductile; in other words, whether it has been burnt.

The structure of a metal is not entirely revealed by the appearance of the fractured surface, as the rupture may occur in the interior of the crystals and indicate a metal with a fine grain. The fracture is generally only crystalline when the metal is formed of fragments of metal feebly held together, and the junction lines of the crystals are the planes of greatest weakness, as in brasses of the third group. Microscopic structure also reveals the cause of the failure of brasses of the first group to roll hot, which is so widely applied in the case of Muntz' metal. We find that the crystal grains of members of the first group, in the case of commercial brass, are more or less separated by the presence of a low eutectic when easily fusible metals, such as lead and tin, are present as impurities. This eutectic alloy, melting at a moderate temperature, would be liquid at the temperature required for hot rolling, and as the grains of the brass are expanded by the heat the fusible alloy can very readily penetrate the junction planes, and so weaken the cohesion as to cause complete separation by the pressure of the rolls. On the other hand, in brasses

of the second group the crystalline grains are not joined together but absorbed in a certain quantity of amorphous matter which the impurities do not seem to affect, hence they can be rolled hot without injury.

# CHAPTER XI.

## GERMAN SILVER.

§ 87. The alloys largely manufactured under this name, consist essentially of nickel, copper, and zinc, but in some cases a little cobalt is added. Iron is usually present as an impurity, and in the case of cast work, 1 to 2 per cent. of lead is often added. The properties which make German silver so valuable are—its white colour, brilliant lustre, hardness, tenacity, toughness, malleability, ductility, and power of resisting certain chemical influences. Cobalt frequently accompanies nickel in its ores, and becomes reduced at the same time as that metal, but as the chemical and physical properties of these metals are closely allied to each other, cobalt does not exert an injurious influence.

Iron has a beneficial effect on German silver for some purposes. It makes the colour whiter, increases the tenacity and elasticity, but makes it harder. In some experiments made by the author, 1 to 2 per cent. of iron was found to have no deteriorating effect, except with regard to hardness, and the colour of an alloy containing 12 per cent. of nickel was equal to one containing 16 per cent., in which no iron was present, the same quantity of zinc being used in each case. The metal rolled remarkably well. In the better qualities of

German silver used for rolling and spinning, iron was found to be injurious, and for these purposes the purer the alloy the better it works. All commercial varieties of German silver contain iron, especially when scrap-metal is used in connection with new metal for the melting charge, the iron being probably obtained from files and other tools used in the fabrication of the various articles. Packfong, the original nickel alloy introduced from China, contains as much as 3 per cent. of iron. Gersdorff states that iron is difficult to alloy with the other constituents, and when that metal is added to fused German silver it does not combine with it, and forms upon the surface of the fused mass a layer, consisting of copper, nickel, and iron. He states that the iron must be previously fused with a portion of the copper, under a layer of charcoal-powder in a blast-furnace, and the alloy formed may then be used to alloy with the nickel, zinc, and the remainder of the copper required. This is quite unnecessary, as proved by the author's experiments, in which copper nickel and the best iron wire were strongly heated together in a covered crucible, and zinc added to the molten contents, then vigorously stirred. The metals were perfectly alloyed together, and no separation of iron could be detected when the ingot was rolled into a thin sheet and highly polished.

The effect of tin when alloyed with German silver to the extent of from 2 to 4 per cent. was found much more injurious than that of iron, the strips being brittle when rolled, and the metal of a decidedly yellow cast when polished. From his experiments the author concludes that there is no advantage in adding tin to German silver, as it impairs the colour, hardens the metal, and makes it brittle. Moreover, tin is an expensive metal, and better effects can be obtained by the use of iron and zinc.

Silver in certain proportions does not impair the

malleability of German silver, but no particular advantage is gained by its use. M. Ruolz many years ago manufactured a series of alloys for jewellery having the following composition:

| | |
|---|---|
| Silver, - - - - - - - | 20 to 30 |
| Nickel, - - - - - - - | 25 to 30 |
| Copper, - . - - - - - | 35 to 50 |

By varying the proportions the alloys may be made to resemble silver very closely; but the nickel and copper must be of good quality, or the alloys will be hard, brittle, and difficult to work.

Modern proportions for German silver alloys vary considerably, but the copper is usually between 50 and 60 per cent., and the nickel, according to the quality of the metal desired, varies from 7 to 30 per cent. The remainder is zinc. In order to get a general idea of the microscopic structure of typical samples of German silver, the author has selected the three following:

| | | | | | |
|---|---|---|---|---|---|
| Copper, | 60 | Nickel, | 12 | Zinc, | 28 |
| ,, | 60 | ,, | 16 | ,, | 24 |
| ,, | 60 | ,, | 20 | ,, | 20 |

In practice the copper varies with each quality, and is generally a little lower than the above proportions, with a consequent increase in the amount of zinc, but it was deemed advisable to keep the copper constant for purposes of comparison.

§ 88. Fig. 73 shows the structure of the 12 per cent. nickel alloy, made in a small crucible and poured into an ingot mould. After polishing, it was etched in hydrochloric acid. There is but a faint suggestion of large polygonal grains, the interior being filled with a very fine network of bright lines, but these are not continuous and appear as a number of dashes with dark spaces between, although when seen with a low power they seem to be continuous. It gives one the impression of two different bodies endeavouring to crystallise together

and mutually interfering with each other. The pattern in some parts consists of rows of septa with others branching from them at right angles. The surface as a whole is fairly uniform, and the interlacing figures suggest a metal of considerable strength. The ground-mass is very fine, and is probably composed of an eutectic mixture of copper and copper-zinc alloy. If this is so, the nickel, probably alloyed with copper, forms the bright network already alluded to. These are probably the skeleton outlines of crystals immersed in a mother-substance, which was the last to solidify.

Fig. 74 shews a portion of the 12 per cent. nickel alloy just described, but it has been raised to a high temperature, sufficient to burn it, but not to melt it. It will be observed that the structure has totally changed, the fine meshwork has entirely disappeared, the substance has undergone re-crystallisation and now presents the appearance of mosaic, with large crystal grains bounded by thin walls. These walls are not uniform, but at frequent intervals contain a second substance which also forms a kind of triangular lake at the solid angles of three contiguous crystals. The interior of the crystals is made up of extremely fine grained material, which, when viewed with a high power, is seen to have the characteristic structure of an eutectic mixture. Scattered over the interior of the polygons are a number of small circular bodies formed of a bright ring with a dark centre corresponding to the boundaries and interiors of the large polygons. The boundary lines of the polygons are evidently the first to crystallise out, and the circular bodies are probably secondary crystals, which at a lower temperature have crystallised out from the mother substance. The fact that the boundary lines of the large polygons are not continuous but frequently separated by a more fusible substance readily explains the weakness of such a structure, and fully accounts for the brittleness inherent in burnt metal,

§ 89. A section from the 16 per cent. nickel alloy presents the same general appearance as that of the 12 per cent. alloy, but with a closer grain. This alloy, highly magnified, is shewn in fig. 75. The same remarks also apply to the 20 per cent. alloy. Burnt samples of the 16 and 20 per cent. alloys shew the same large crystal grains bounded by thin walls as that of the 12 per cent. alloy. Fig. 76 shews such a section of German silver with 20 per cent. nickel.

§ 90. Another set of samples was made in the same way as the previous set, but while the same proportions of nickel were used, the proportions of copper and zinc were different, thus:

| | | | | | |
|---|---|---|---|---|---|
| Copper, | 50 | Nickel, | 12 | Zinc, | 38 |
| ,, | 50 | ,, | 16 | ,, | 34 |
| ,, | 50 | ,, | 20 | ,, | 30 |

The object of these experiments was to ascertain whether any material difference in structure was made. Fig. 77 shews the 12 per cent. alloy, etched as before. The whole surface presents the same general dendritic structure as before, but the grains are larger, and distributed over the ground are a number of large fern-like bodies presenting numerous right angles. A portion of this alloy was strongly annealed, when a very decided pattern presented itself after polishing and a slight etching. This is shewn in fig. 78. The fine fern-like structures, as seen in the unannealed section, have been replaced by similar figures having a very coarse grain. Some of these grains occupy an isolated position, while others are much more elongated and form a connected part of the general framework. Segregation has evidently occurred, forming homogeneous grains of what appears to be structureless matter embedded in a fine ground-mass of a granular eutectic. Had the temperature been raised higher, or the time of annealing been pro-

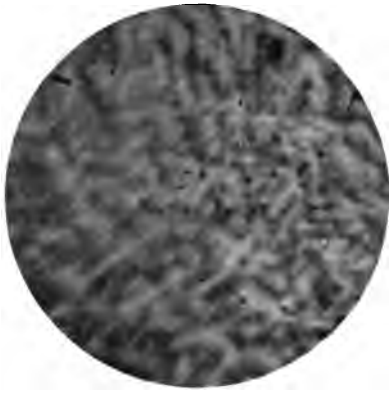

FIG. 75. German silver with 16°/₀ nickel. ×200 dia.

FIG. 76. German silver with 20°/₀ nickel, after burning. ×50 dia.

FIG. 77. German silver with 12°/₀ nickel and 50°/₀ copper. ×50 dia.

FIG. 78. German silver with 12°/₀ nickel, strongly annealed. ×50 dia.

longed, the grains would have united to form another series of larger grains of a different composition, as seen in burnt metal before alluded to. In the present section fine boundary lines are faintly seen, which doubtless would increase and thicken as well as deepen with a continuance of the high temperature. Three distinct bodies are therefore present. The prominent dendrites of what I take to be a copper-nickel alloy, the eutectic of copper and copper-zinc alloy, and the boundary lines of what is probably a chemical compound such as $CuZn_2$.

The corresponding 16 and 20 per cent. alloys shew no special distinguishing features from the above.

# CHAPTER XII.

## GOLD. SILVER.

§ 91. **Gold.**—Gold is usually found in the metallic state in nature (generally associated with silver, and sometimes with copper, iron, and platinum). It is often found in ores of lead, zinc, iron, and copper. Gold is a yellow metal, with a brilliant lustre; it exceeds all others with regard to malleability and ductility; its specific gravity is 19·32; its melting point is 1061° C.; and it is only volatile at very high temperatures. It is almost as soft as lead, and can be welded by pressure in the cold; it is one of the best conductors of heat and electricity. It has a tensile strength of about 7 tons per square inch in the cast state, but this is considerably increased after rolling or drawing. Pure gold is too soft for general use, so that it is usually alloyed with silver and copper, which harden it, without seriously impairing its malleability and ductility. Antimony, tin, and lead are most injurious substances in gold, even when present in minute quantities. It is improved for manufacturing purposes by alloying with certain other metals, such as silver and copper, in small quantity. The great value of gold is the reason, in most cases, why the proportion of added metal should be small. Many metals not only reduce the value of gold, but impart qualities which

U of M

FIG. 79. Pure gold, without polishing or etching. ×30 dia. Oblique illumination.

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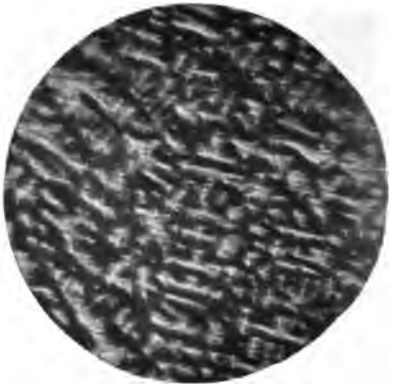

FIG. 80. Gold with 0·5% bismuth. ×50 dia.

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FIG. 81. Gold with 0·5% antimony. ×50 dia.

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FIG. 82. Gold with 0·5% aluminium. ×50 dia.

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destroy its high malleability and ductility, while others render the gold unfit for any useful purpose. With a few exceptions, it may be stated that the higher the value of a metal, the greater should be the proportion of this metal in the alloy

Taking into consideration its high intrinsic value, gold may be considered the most perfect of all the metals, but it is necessary to impart to it a greater degree of hardness than it alone possesses, for the manufacture of coins, medals, jewellery, etc. Silver and copper are the metals invariably used for this purpose, and, when added in small quantity, do not materially alter the malleability and other working properties of gold, but increase its fusibility. The above remarks are only true when the silver and copper employed for alloying are practically pure, as a small quantity of lead, tin, antimony, etc., in the copper would considerably reduce the malleability and ductility of the alloy.

When gold is pure, or as nearly pure as it can be obtained for commercial purposes, it is commonly expressed as fine gold or 24 carat fine, the pound or 1000 parts being divided into 24 equal parts. Thus, 22-carat gold signifies that in 24 parts there are 22 parts gold and 2 parts of other metals. 9-carat gold likewise contains $\frac{9}{24}$ gold and $\frac{15}{24}$ other metals. The metal or metals added to gold are technically termed the alloy.

§ 92. The microscopic structure of pure gold, fig. 79, shows well-defined large crystals with sharp angles, the faces of which show different shades of colour, from yellow to almost black. This is probably due to the presence of small secondary crystals, apparently cubes and octahedra, for it is well known that gold crystallises in the cubic system, being found native in this form. Professor Arnold [1] says that "the structure of chemically pure gold consists of primary, secondary, and possibly

[1] *Engineering*, Feb. 7th, 1896.

tertiary crystals, and it is necessary to recognise the fact that the cohesion between the facets of the crystals is not necessarily equal to the molecular cohesion; indeed there is little doubt that the mechanical properties of a pure metal are mainly determined by the cohesive force acting between the primary crystals. The idea that intensely crystalline metals are necessarily brittle is, therefore, erroneous; for instance, slowly cooled bars of pure gold are built up of very large and geometrical primary crystals, yet such bars are so ductile that it is difficult to break them under severe and repeated flexions."

"The addition of 0·2 per cent. of silver to gold does not alter the structure of the metal last named, nor is it influenced even by the addition of 0·5 per cent. of silver. Either the silver dissolves in the gold without combination, or the gold-silver alloy formed is scattered throughout the mass in isomorphous secondary crystals, incapable of microscopic discrimination. The addition of 0·2 per cent. of copper does not, at low powers, produce any visible change in the structure of the gold: but with high powers isolated crystals of a gold-copper alloy appear to be present. In an alloy containing 0·5 per cent. of copper such is undoubtedly the case, because, scattered thoughout the secondary crystals of the gold, larger and redder crystals of a gold-copper alloy are present in considerable numbers."

These facts give special significance to the action known as "colouring of gold." This operation consists of imparting a colour to gold articles after every other process has been completed. It is stated that its object is to give to alloyed gold all the appearance of fine gold itself by dissolving out the base metal from the surface of the articles and leaving a facing of gold of a deep rich colour. This is only partially true, as some of the gold is also dissolved. Moreover, pure gold is of a pale yellow colour, and the tint of coloured gold is

generally a reddish yellow, showing that the surface cannot be pure gold. The special attraction of coloured gold is the rich dead appearance due to the uniform matting of the surface by the solvent action of the acid. Two distinct modes of colouring are adopted by jewellers, termed respectively *dry colouring* and *wet colouring*. The latter is most frequently practised, as the former cannot well be applied to gold inferior to 18 carat. If, therefore, gold-copper alloys are composed of gold with an alloy rich in copper disseminated through the mass, it is easily seen why the colouring liquid exerts a selective action and also why the rich dead appearance is produced.

§ 93. Gold containing a small quantity of bismuth is characterised in a microscopic section by large polyhedral grains, with thick walls, which doubtless contain a fusible bismuth alloy. It will be observed that the strictly geometrical forms of pure gold have been entirely altered. The bismuth alloy not only breaks up the gold crystals into smaller ones, the planes of which have become rounded, but also penetrates the substance of the crystals in an irregular manner, producing streaks and blotches. These being more soluble than that of gold are more readily removed by the etching liquid, which, in the case of gold, is aqua-regia. That the adhesion of the bismuth alloy to the crystals of gold is small is proved by the extreme brittleness of the mass, which is entirely due to the bismuth alloy, as the separate crystals of gold are malleable. An example of gold with 0·5 per cent. of bismuth is shewn in fig. 80.

§ 94. The presence of antimony in gold increases the hardness and tenacity, but this is done at the expense of ductility and malleability. Antimony has a strong affinity for gold and dissolves it readily. Melted gold dissolves the vapour of antimony, and even 0·05 per cent. hardens it. An alloy of 9 parts gold to 1 part

antimony is white and brittle, with a granular-crystalline appearance when fractured. The microscopic structure of gold with 0·1 to 0·2 per cent. of antimony reveals the presence of a fusible gold-antimony alloy, which breaks up the large crystals of gold into smaller and irregular rounded grains, forming a meshwork around them. These doubtless are planes of weakness, which accounts for the brittleness. The boundary lines are fairly thin in parts, but run into parts of much greater thickness, with a considerable widening out at the junction of three crystals, forming a miniature lake of antimonial matter. In some cases the antimony alloy segregates in patches and may fill up the body of the crystal grain completely. Fig. 81 shews gold with about 0·5 per cent. of antimony.

§ 95. Gold and aluminium alloy well together, and, when cold, the alloys show a marked granular structure. Gold with 0·2 per cent. of aluminium casts very sound. A microscopic section of this impure gold indicates the presence of secondary crystals of a gold-aluminium alloy as well as a meshwork of the same, which somewhat modifies the shape of the primary crystals and tends to segregate in patches. Gold and aluminium are remarkable for the number of chemical compounds they are capable of forming, among which may be mentioned the beautiful purple compound, $AuAl_2$. In consequence of this active chemical combination in different proportions we get three or four eutectic mixtures at different temperatures in the various alloys. When gold-aluminium alloys are polished on dry emery or rouge they acquire a more or less golden tinge, and show under the microscope smears of gold, or a pattern of gold, on white or purple; and in cases where the polishing leaves a pitted appearance, the pits are full of gold. On the other hand unpolished alloys are white, if they contain more than 3 per cent. by weight of aluminium, except in the neighbourhood of the compound $AuAl_2$, when the

alloys are purple.[1] Fig. 82 represents a section of gold containing 0·5 per cent. of aluminium which has been etched in aqua regia. The cell walls are very uncertain in outline and appear to have been imperfectly formed, or, if formed, some of the material has broken away during the subsequent cooling and the *debris* scattered over the mass of the crystal grains. From the microscopic structure it may be inferred that this small amount of aluminium in gold does not produce brittleness, as is the case with bismuth and antimony.

§ 96. Osmond and Roberts-Austen[2] have examined gold to which 0·2 per cent. of various metals have been separately added, such as potassium, bismuth, zirconium, lithium, zinc, antimony, aluminium, etc., and conclude that the tenacity varies with the atomic volume of the added impurity. The samples were afterwards submitted to microscopic examination. From the results the authors conclude that there is no relation between the structure, the appearance of the fractures, the melting points of the alloyed elements, and the mechanical properties of the alloyed gold. With respect to eutectic alloys which may act as a cement, it is claimed that there is no evidence that they exist in ten out of the twelve alloys examined. Small secondary crystals show themselves and might be taken for eutectics, but they occur everywhere, and in all cases with identical appearances, forms, and dimensions. They are collected into crystallites, which pervade the whole mass. They are, therefore, due to the crystallisation of the gold itself, although the alloying substances sometimes join up the crystals in question.

§ 97. **Silver.**—Silver is remarkable for its whiteness and brilliant lustre, although when precipitated from its solutions it often forms a grey powder; it is harder than

[1] *Phil. Trans. Roy. Soc.*, vol. 194, pp. 201-232.
[2] *Phil. Trans. Roy. Soc.*, vol. 187, pp. 417-432.

gold, but softer than copper, the relative hardness being as 4 : 5 : 7·2. Silver is extremely malleable and ductile, with a tenacity of about 7 tons per square inch, and it elongates 30 per cent. before rupture; its specific gravity is 10·5, which may be slightly increased by the operations of coining, rolling, hammering, etc.; it melts at 960° C., is the best conductor of heat and electricity, is volatile at high temperatures, and at the temperature of the electric arc it may be boiled and distilled. When heated in a current of hydrogen it volatilises at 1330° C.

Silver is too soft to be worked by itself for most purposes, pure silver being only used in special cases, where the presence of another metal would exert an injurious effect. In most cases, silver is alloyed with copper, and occasionally with other metals, as in silver solders.

Silver is capable of absorbing oxygen and other gases, and retaining them when cold, by heating the metal to redness in contact with oxygen or other gas. Such gas is said to be *occluded*. Graham found that pure silver occluded ·545 of its volume of oxygen; and fine silver wire ·002 inch diameter, yielded ·289 of its volume of a gas, consisting chiefly of carbonic acid. When standard silver is heated to low-redness it becomes almost black on the surface, from the oxidation of the copper. Silver wire thus blackened was found to have occluded several times its volume of oxygen. Fine silver wire heated to redness in hydrogen, and cooled in that gas, occludes ·211 of its volume of hydrogen.

§ 98. Silver and sulphur readily combine at a red heat to form the compound $Ag_2S$. This compound may be dissolved in an excess of silver and act as an injurious constituent. The microscopic structure of silver containing about 0·3 per cent. of sulphur is seen in fig. 83. There is an absence of the large hexagonal plates, so

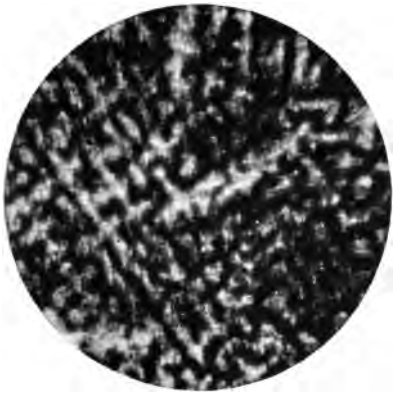

FIG. 83. Silver with 0·3% sulphur. ×50 dia.

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FIG. 84. Pure silver, without polishing or etching. ×50 dia.

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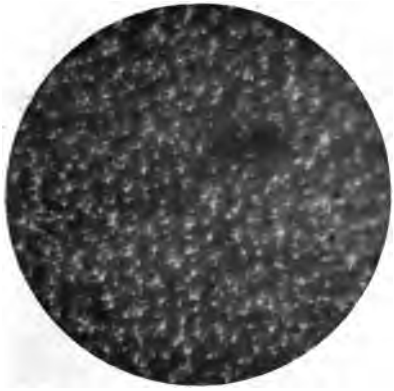

FIG. 85. Silver with 0·3% arsenic. ×50 dia.

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FIG. 86. Silver with 0·3% antimony. ×50 dia. Strongly etched.

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conspicuous in pure silver, as though the sulphur compound had broken them up and segregated in small dots and patches, forming a heterogeneous mixture of silver and silver sulphide.

§ 99. The structure of pure silver (fig. 84) is much the same as that of gold, and the most of the remarks made with respect to pure gold apply equally to that of silver; also the effect of copper on silver is analogous to the influence of that metal on gold. These metals unite in all proportions, forming a series of most valuable alloys, having a great variety of applications in the arts. Combination takes place with expansion, so that the specific gravities are less than the mean of their constituents. Most of the alloys are as ductile as silver, and possess more hardness, elasticity, and sonorousness. The colour of these alloys is white until the copper reaches nearly 50 per cent. and beyond that the colour is yellowish, up to about 70 per cent. copper, when a red tint prevails The hardest alloy is that containing 5 parts by weight of silver to 10 or 11 parts copper.

Professor Roberts-Austen has determined the melting points of certain silver-copper alloys, and states that the alloy containing 630·29 of silver per 1000 of alloy, and represented by the formula AgCu, has a lower melting point than silver, or than any other alloy of silver and copper.

§ 100. **Arsenic** unites with silver to form a series of hard, grey, brittle, and fusible alloys. Fig. 85 is silver containing 0·3 per cent. arsenic. It has a frosted appearance when seen with the naked eye, which under a high power is resolved into a fine continuous network of small elongated grains of uniform size, and so joined together as to form a series of parallel lines. The boundaries of the silver crystals are faintly seen, but the interiors are filled with the granular structure above

mentioned. The grains all run in the same direction in the same crystals, but are arranged at an angle to those in the contiguous crystals. This structure should give increased strength to silver.

§ 101. **Antimony** unites with silver in all proportions, and, when the antimony is present in more than minute quantities, produces hard, white or grey, and brittle alloys. Fig. 86 shews silver with 0·3 per cent. of antimony. It consists of a fine, very irregular meshwork, the walls of which vary considerably in thickness and are very diverse in structure. For the most part the walls have a compound structure containing silver, which in places is completely enclosed by thin walls, forming a series of small lakes. In other parts these patches are made up of small parallel striae suggesting an eutectic mixture. Hence three distinct substances are probably present—silver, antimonide of silver, and the eutectic formed of these two.

§ 102. **Bismuth** seems to be very injurious to silver, as indeed it is to all malleable metals. Fig. 87 shews silver with 0·3 per cent. of bismuth. It is made up of irregular polyhedral grains of a comparatively large size, so that they may be seen even with the naked eye. The boundary walls are thin in places, while in others they appear much wider with a more distinct outline. On magnifying these parts to 200 diameters they are found to be composed of disconnected patches, some of which are evidently small crystals. These are probably secondary crystals, formed during the cooling, which explains the broken nature of the boundary walls. In some places small patches of the bismuth compound have diffused into the body of the crystal grains. Altogether the meshwork is of a very disunited character, the secondary crystals seem to lack cohesion, and the cause of the brittleness of silver containing bismuth is very easily explained.

FIG. 87. Silver with 0·3% bismuth. ×50 dia.

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FIG. 88. Silver with 0·5% aluminium. ×50 dia.

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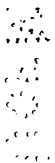
FIG. 89. Silver with 0·5% tin. ×200 dia.

Page 141.



§ 103. **Aluminium** alloys with silver, making it harder. Fig. 88 shews silver with 0·5 per cent. of aluminium. It has a somewhat frosted appearance in consequence of the dendritic structure which uniformly covers the whole surface. The crystals, or rather skeleton outlines of crystals, are formed of rectilinear rods or septa, with similar rods crossing the former, and again from these longer rods are projected smaller ones also at right angles. In some parts these smaller rods terminate in sponge-like masses filled with granular matter. The whole presents a very chequered appearance, and the septa are fairly uniform in thickness. Silver with this proportion of aluminium should possess great strength, for the septa seem to completely interpenetrate, showing no signs of division or cleavage planes.

§ 104. **Tin** alloys with silver in various proportions forming hard and brittle alloys. Fig. 89 shews silver with 0·5 per cent. tin. The structure closely resembles the preceding sample, containing aluminium, having a dendritic structure with rectilinear septa at right angles, but the ground-mass is granular and more apparent.

# CHAPTER XIII.

## MISCELLANEOUS ALLOYS.

§ 105. It may be remarked that the difficulty of polishing soft metals and alloys so as to obtain a smooth surface free from scratches is much greater than with hard metals, and requires the very softest chamois leather and the very finest rouge for finishing. In the case of many alloys of the softer metals much valuable information as to their constitution is obtained during the polishing process, inasmuch as some of the constituents are harder than others, and therefore rub down unequally, the harder parts standing out in relief. When hard crystals thus reveal themselves in an alloy of soft metals, we may suspect that a chemical compound of the constituents is present. This is the case with copper-tin and silver-tin alloys. The relative hardness may be tested by scratching with a hard needle. A want of homogeneity is often betrayed in polished specimens by differences of tint. Thus certain copper-antimony alloys give a violet colour, due to the presence of the combination known as *regulus of venus*. Polished specimens may also be coloured by heating, termed heat-tinting. Copper changes from light red to dark yellow, followed by orange and then green. The patterns obtained by heating are often analogous to those

produced by etching, and by combining the two methods striking effects may be obtained. First, slightly etch the metal, and then gradually heat, but the surface must be perfectly clean and dry before applying the heat, which must be done on a hot plate or in an air bath, and not in contact with a flame.

The preliminary work may be done on a very fine smooth file, followed by rubbing on a smooth oilstone, using clean water in place of oil, so as to obliterate the file marks. The section is then rubbed on a sheet of French emery paper, No. 0000, using the very lightest pressure; otherwise the softer parts of the metal will be dragged and torn, and overlap the harder parts. The finishing touches are given on a smooth cloth, with a little of the very finest rouge kept constantly moist. The surface must be frequently inspected, and the polishing stopped immediately the scratches are removed. If the action is carried beyond this point the softer constituents will be carried away, and the crystals of the harder substance, instead of being sharp, will become rounded.

M. Osmond, in his paper on Metallography read before the International Congress at Chicago, gives the observations of M. Guillemin: "Micrographic examination permits the direct classification of the usual alloys in a few categories, thus:

Tin-bronzes.
Phosphor-bronzes.
Brasses containing less than 37 per cent. of zinc.
Aluminium bronze.
Aluminium brass.
Delta metal.
Roman bronze, etc.

"In the white anti-friction alloys containing tin, antimony, and copper, it is easy to recognise the presence, and, even with a little practice, to make a close estimate

of the proportion of lead. By examining the ingots of copper composing different casts from the same smelting of ore, those which have been perfectly refined can be distinguished, and the rest can be classified according to the degree to which they have been refined. It is known that the mechanical properties of brasses and bronzes are profoundly modified by the addition of small quantities of phosphorus and of aluminium. The presence of these two elements can be determined with certainty by micrographic examination. Thus, the tracings assume invariably the forms of veins in marble when the alloy contains aluminium, even in portions so minute as to be detected with difficulty by chemical analysis. In like manner, phosphorus produces in tin-bronzes an absolutely characteristic image, recalling a fern-leaf. This reaction is, however, marked by the presence of over 4 per cent. of zinc. Finally, for a known alloy, the micrograph indicates also the conditions of casting, as well as the nature of the mechanical work subsequently performed upon the specimen. Thus the image shows whether the metal has been cast too hot or too cold, whether it has been stamped or rolled."

§ 106. An explanation of eutectics has already been given, and in most alloys eutectics can be discovered by microscopic investigation. Charpy[1] examined many alloys for this purpose and obtained valuable information as to their constitution. He first prepared an alloy of bismuth and tin, containing 46·1 per cent. of bismuth and 53·9 per cent. of tin. The alloy was melted and allowed to cool slowly; when the greater part had solidified the remaining liquid part was poured off, which was the eutectic mixture. The metal was then etched in very dilute hydrochloric acid, which only attacks the tin. The section showed that the two metals were simply joined together, but so closely packed as to

[1] *Soc. d'Encour. pour l'Indus.*, March, 1897.

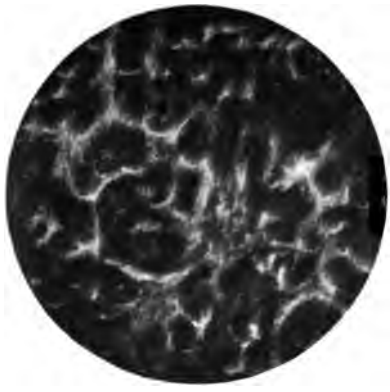


FIG. 90. Bismuth with 54°/₀ tin. ×200 dia.

FIG. 91. Silver with 34°/₀ antimony. ×200 dia.

FIG. 92. Antimony with 30°/₀ lead. ×50 dia.

FIG. 93. Bismuth with 40°/₀ tin. ×200 dia.

require high magnifying power to reveal the structure. Fig. 90 shows a section magnified to 220 diameters; the white parts correspond to bismuth and the black parts to tin which has been attacked by the acid. The striated parts, alternately black and white, are the eutectic. This is only shown thus when the metal is cooled slowly, but when cooled quickly the whole surface is striated, and exceedingly fine. In the slow solidification it seems to produce at first a separation of some parts rich in tin and in other parts rich in bismuth. In each of these portions the metals separate in laminae. This finely striated appearance is characteristic of eutectic alloys.

§ 107. Fig. 91 shews an alloy of 66 per cent. silver and 34 per cent. antimony. This section was polished and treated with dilute nitric acid, which dissolves the silver and covers the antimony with a layer of the white oxide; the black parts correspond to silver or a rich silver alloy, and the white parts to antimony. The large crystals of silver or silver alloy are embedded in the eutectic, which is distinguished by the usual striae. Instead of using nitric acid as a separator, sulphuretted hydrogen may be employed, which blackens the silver and does not affect the antimony.

§ 108. Alloys containing lead and antimony show very interesting examples of crystallisation, in which hard crystals are embedded in a more fusible eutectic alloy. The proportion of hard crystals varies regularly with the amount of antimony, and are clearly shown after polishing. The eutectic is revealed by etching with dilute nitric acid. Fig. 92 shews an alloy with 70 per cent. antimony and 30 per cent. lead, showing large and hard crystals of antimony embedded in an eutectic alloy.

§ 109. Another alloy which shews large crystals of one metal in a matrix consisting of an eutectic alloy is tin with 60 per cent. of bismuth, see fig. 93. This effect is

produced by polishing, the white crystals of bismuth standing out prominently from the eutectic matrix.

§ 110. A striking analogy to alloys of tin and bismuth is found in steel, which, with 0·89 per cent. of carbon, is seen to be composed of pearlite, see fig. 5, an intimate mixture of ferrite and cementite in alternate layers. This is the eutectic alloy. In all cases where the constituents of the eutectic are alternately hard and soft the structure is revealed by polishing and etching, exhibiting the characteristic pearly appearance. Another excellent instance of this is the alloy consisting of 80 per cent. lead, 5 per cent. tin, and 15 per cent. antimony.

§ 111. There are three normal types of binary alloys which may be suitably studied by microscopic examination with great profit: (1) The two metals yield neither definite combinations nor isomorphous mixtures, such as lead-tin, tin-bismuth, and antimony-lead; (2) the metals yield a definite compound, such as antimony-copper and nickel-tin; (3) the two metals form isomorphous mixtures such as bismuth-antimony. In each of these cases, at the moment of solidification, we may have deposited either a pure metal or a definite compound; generally this separation of a definite substance tends to change the composition of the remaining liquid portion, and the separation can only continue if the temperature is being lowered. Theoretically, this would manifest itself by a total difference of composition in different parts of the ingot after solidification. Practically these differences are generally very small in consequence of crystallisation of films, or very fine needles, which form a network in the still liquid portion, and so entangle each other as to render their separation according to their densities impossible.

In the case of alloys yielding definite compounds there will be two eutectics, each intermediate between

FIG. 94. Antimony with 40°/₀ bismuth. ×50 dia.

FIG. 95. Antimony with 10°/₀ copper. ×50 dia.

FIG. 96. Copper with 15°/₀ antimony. ×50 dia.

the definite compound and one of the pure metals, as in the case of copper-antimony alloys. If there are two definite compounds there will be three eutectics, as in the case of copper-antimony alloys.

As an example of an alloy composed of isomorphous mixtures we may take bismuth-antimony. The hardness varies directly with the composition, and this continuity is seen in the micro-structure. In all the alloys the crystals vary slightly in form as the bismuth or antimony is increased, but are too ill-defined to measure the angles. The alloys of bismuth and antimony reveal one peculiarity characteristic of isomorphous mixtures, viz., the structure is revealed by polishing, the hard parts being in relief, the crystals being rounded and comparable to a chain of mountains. Probably, at the moment of solidification, there is formed a fern-like framework of crystals of antimony, which is the least fusible of the two metals, and these crystals grow afterwards by a disposition of the two metals, in which the amount of bismuth gradually increases. Oxidation by heat, by nitric acid, or by electrolysis confirms this supposition. We see the effects of oxidation first in the depressed parts, those which have been most removed by the polishing, and this action is continued until the whole surface is gradually covered without any intermission. Fig. 94 shews an alloy of 40 per cent. bismuth polished and etched, the white parts are the hardest portions and the dark groundwork the most fusible, and therefore the richest in bismuth, as shown by gradually raising the temperature until little globules of metal are formed.[1]

§ 112. Alloys of copper and antimony afford a good example of metals which form a chemical compound, the formula for which in this case is $SbCu_2$. They may be conveniently divided into four classes: (1) with 0 to

[1] Charpy, *Bull. d'Encour. pour l'Indus.*, March, 1897.

25 per cent. copper; (2) with 25 to 60 per cent. copper; (3) with 60 to 70 per cent. copper; (4) with 70 to 100 per cent. copper. The alloys of the first series contain hard crystals of antimony embedded in an eutectic alloy. The structure is revealed by simple polishing and intensified by etching with dilute hydrochloric acid. Fig. 95 shews an alloy with 10 per cent. of copper, the crystals of antimony showing white. As the amount of antimony is increased the crystals become less, but of the same shape. The second series of alloys, containing 25 to 52 per cent. of copper, are formed of crystalline grains, which appear violet after polishing and located in a characteristic eutectic alloy, well seen after etching with hydrochloric acid. These grains increase with the percentage of copper, and when 51·5 per cent. is reached they cover the whole surface. This is the chemical compound $SbCu_2$. In the third series, with upwards of 52 per cent. of copper, and up to 70 per cent. the general tint is still violet, but under the microscope we see crystalline grains of a violet colour and a residue formed of small white crystals, some of which penetrate the violet grains. The latter are surrounded by a thin network, some of which is also seen in the interior of the large crystalline grains. This is probably the second eutectic. A similar structure is found in 10 per cent. aluminium bronze and in brazing solder. In the fourth series, with upwards of 70 per cent. of copper, the structure is revealed by simple polishing. On heating in air prominent crystalline grains are the first to be oxidised. Fig. 96 shews the general structure of an alloy with 85 per cent. of copper after polishing and heating. The dark parts are probably dendrites of pure copper separated by the contours of the eutectic alloy, shewn white in the figure.

# GLOSSARY.

§113. **Acicular.** A term used to signify fine needle-shaped bodies.

**Allotropic.** When an element occurs in more than one form the word allotropic is used to express those varieties which are different from the normal form.

**Allotropy.** Roberts-Austen defines it as a change of internal energy occurring in an element at a critical temperature, unaccompanied by a change of state. It is the power to undergo chemical and physical change without change of composition.

**Alloy.** An intimate union of two or more metals, and may be a mixture, a chemical compound or a solution.

**Alpha iron.** The supposed normal condition of iron below 700° C. after allowing it slowly to cool. It crystallises in the cubic system and is magnetic.

**Amorphous.** Without any definite crystalline form.

**Arborescent.** An appearance roughly resembling fir trees or ferns, often seen in the structure of metals. Also in slags.

**Austenite.** A constituent of hard steels produced by very rapid quenching from a high temperature.

**Beta iron.** The supposed condition of iron at temperatures between 750° and 860° C. It is isomorphous with alpha iron and non-magnetic.

**Blowholes.** Bubbles of gas enclosed in solidified metals.

**Botryoidal.** Consisting of spheroidal aggregations somewhat resembling a bunch of grapes.

**Brittle.** Easily broken. It is due to lack of cohesion between the cleavage planes or between the joints of crystals which may be impregnated with impurities.

**Burnt (metal).** Applied to metal which has become brittle by excessive heating. It is generally highly crystalline or coarsely granular.

**Capillary.** Having a hair-like structure.

**Carbide carbon.** Commonly termed combined carbon. It has the general chemical formula $M_3C$.

**Carbon, hardening.** The condition of carbon which imparts hardness to hardened steels.

**Carbon, missing.** That carbon in hardened and tempered steels which does not give a colour to nitric acid.

**Carbon, temper.** The finely divided carbon which separates from cast iron and some steels during prolonged annealing. It is better defined as annealing carbon.

**Cellular.** Containing cavities or cells resembling a network.

**Cementite.** Carbide of iron, having the formula $Fe_3C$. and containing 6·7 per cent. of carbon. It is the hardest constituent of ordinary steel.

**Cleavage.** Tendency to cleave or separate along definite planes in the mass of a crystal or crystal grain.

**Cohesion.** The force by which particles of matter are held together.

**Cold-short.** The brittleness of a metal when worked cold.

**Columnar.** Having a structure roughly resembling prisms.

**Conchoidal.** When a body breaks in the shape of a shell it is said to have a conchoidal fracture.

**Constituents.** As applied to metallography are the structural parts of an alloy or metallic substance. Also termed Minerals.

**Critical points.** The temperature at which a chemical or physical change occurs in heating or cooling a body. If the change does not occur at one fixed point, but extends over several degrees, this range is termed a zone.

**Crystal.** A definite geometrical solid, having invariable angles, developed from a fluid or from a liquid or solid solution.

**Crystal grain.** Grains of metallic matter having a crystalline structure but devoid of crystal faces and angles. Some metallographists term it simply granular.

**Cryptocrystalline.** A general term used to denote mere traces of crystalline structure.

**Crystalline.** A confused aggregate of imperfectly formed crystals.

**Crystallised.** The condition of a body which has developed crystals from some other condition.

**Crystallite.** An imperfect crystal.

**Dendritic.** Tree-like or moss-like. Similar to Arborescent.

**Drusy.** Cavities containing crystals.

**Etching.** Treatment of a polished surface by liquids or by gases, with or without heat, so as to produce a differential action and thus reveal the presence of different constituents.

**Etching figures.** These are produced by excessive etching, so as to produce pits, which often reveal the true crystalline structure.

**Eutectic.** In most alloys and impure metals there is generally formed one mixture of the constituents which has a lower freezing point than those of any other proportions, and termed the eutectic alloy. It is also termed the solidified mother liquor. Eutectic alloys in polished and etched surfaces of metals often present the appearance of mother-of-pearl when obliquely illuminated. When an alloy consists entirely of the proportions which form the eutectic mixture it has only one freezing point.

**Face.** The bounding plane surfaces of crystals.

**Ferrite.** A term used to signify pure iron. It is also used for iron alloys, such as silicon-iron, nickel-iron, etc., which contain no carbide. It would be better, however, to add a perfix and term them silicon-ferrite, nickel-ferrite respectively. It is the softest constituent of steel and cast iron, and yields cubical etching figures.

**Fibrous.** Consisting of fibres or threads, such as wrought iron.

**Fracture.** The broken surface of a body. It may be conchoidal, even, rough, hackly, earthy, fibrous, granular, or crystalline.

**Freezing point.** The temperature at which a metal solidifies from the liquid condition.

**Friable.** Easily reduced to powder or crushed.

**Gamma iron.** The supposed allotropic condition of iron at temperatures above 850° C.

**Glass-hardness.** The greatest degree of hardness of which steel is capable.

**Gliding plane.** The direction in which the molecules glide over each other in a crystal under pressure.

**Grain.** A particle of matter, whether crystalline or not, in which no definite crystal faces or angles are apparent.

**Granular.** A structure that appears to be composed of grains.

**Ground-mass.** The matrix in which crystals are embedded. In some cases the matrix appears structureless, but more often it shows a structure characteristic of an eutectic. Sometimes it is minutely crystalline.

**Hackly.** Rough, coarse grained, with sharp angular points.

**Hardening.** 1. Sudden quenching of steel from a strong red heat. 2. The slow cooling of certain alloys, such as manganese steel.

**Hardness.** The degree of resistance offered by a body to the separation of its particles. It is generally measured by noting the force required to scratch a body with a steel or diamond point.

**Heat-tinting.** Heating the polished surfaces of metals in air

or other gases in order to produce different colours on the various constituents.

**Honeycombed.** Containing blowholes due to presence of gases.

**Hot-short.** The brittleness of a metal when worked hot.

**Hysteresis.** The persistency with which certain bodies tend to retain a previous condition.

**Inclusions.** Foreign matter mechanically enclosed in metals.

**Intercrystalline.** Space between any two adjacent crystal grains.

**Intergranular.** Similar to intercrystalline.

**Interpenetration.** The passage of foreign matter between crystal faces, causing their separation.

**Isomorphous.** Crystals of different bodies which have the same form.

**Joint.** The plane of junction of two crystal grains.

**Lamellar.** Consisting of thin plates.

**Lamina.** Similar to lamellar.

**Lattice structure.** Network of crossed lines.

**Lenticular.** Lens-shaped.

**Liquation.** The separation of one constituent of a body by flowing when in the liquid or semi-liquid state.

**Lustre.** The character of the reflected light from the surface of a body.

**Macroscopic.** A structure visible to the naked eye. Used in contradistinction to microscopic.

**Magma.** The molten mass or paste, which on solidification forms a solid alloy, or mixture of metals.

**Martensite.** The constituent of hardened steel, consisting of interlacing rectilinear fibres, which gives to the structure great hardness.

**Massive.** In tufts or masses, not stratified.

**Matrix.** See ground-mass.

**Metallography.** That branch of metallurgy which describes the structure of metals. It also may include the composition, constitution, and physical properties.

**Metallurgy.** The art of extracting and working metals, and the scientific principles involved.

**Melting point.** The temperature at which a solid body melts.

**Mixed crystals.** A term used for a homogeneous substance containing crystals of different bodies.

**Mother liquor.** The portion of a solution which remains liquid after the other constituents have solidified by crystallisation.

In most alloys and metallic mixtures the mother liquor is the eutectic constituent.

**Orientation.** The relative directions of the axes of crystals.

**Pearlite.** The constituent of steel which consists of an intimate mixture of ferrite and cementite. Steel with 0·89 per cent. of carbon consists wholly of pearlite.

**Phase.** A mass chemically or physically homogeneous. The state of a phase is determined if the pressure and temperature, together with the chemical potential of its components, be known. In physical chemistry the term means homogeneous particles within a body, separated by dividing surfaces from the other parts. Examples of phases in steel are: ferrite, martensite, and cementite, while pearlite contains two or three phases: viz., ferrite, cementite, and sorbite.

**Pipe.** A central tube or cavity in the upper part of an ingot of metal.

**Polish attack.** The developing of the harder constituents of an alloy by friction of rubbing on soft pads. The softer parts being rubbed away most, leave the harder parts in relief.

**Polish etching.** The combined effect of friction and a liquid on a metal when polished on parchment, moistened with an etching liquid.

**Polishing.** The final operation on the surface of a metal for producing a bright surface and removing the final scratches.

**Polyhedral.** Applied to crystal grains having two or more different shapes.

**Polymorphism.** When a body is capable of assuming more than one molecular form.

**Prismatic.** Crystals in the shape of prisms or columns.

**Pseudomorphous.** The form of a body not belonging to it, produced by displacement or alteration of some kind.

**Radiating.** When fibres are arranged around a central point like the spokes of a wheel.

**Recalescence.** The evolution of heat at a critical point. Applied to steel when cooling and the carbon changes to the cement form.

**Red-short.** The brittleness of metal when worked at a red heat.

**Reticulated.** Like a net, with crossed lines.

**Rotation effect.** The varied illumination of crystal grains on the etched surface of metals on rotating the section while viewing it under the microscope.

**Scaly.** In plates, which overlap each other, like the scales of a fish.

**Scoriaceous.** The appearance of slag when included in metals.

**Scoriae.** Cinder or slag.

**Seam.** An elongation of a blowhole by mechanical treatment, such as rolling.

**Segregation.** A gathering together of certain constituents in certain portions of the mass. These are generally the more fusible portions of the constituents and therefore the last to solidify.

**Short.** See cold-short, hot-short, and red-short

**Skeleton crystals.** The framework of crystals before the perfect form is developed.

**Slag.** The fusible compound formed to take up impurities from metaliferous matter. It is generally a silicate, and in most cases the waste product of an operation.

**Slip bands.** A microscopic appearance of metals after straining by tensile stress, caused by the crystal grains gliding along the cleavage planes.

**Solid solution.** Two or more homogeneous bodies in the solid state. When crystalline, the mass consists of ismorphous mixtures or mixed crystals.

**Solution plane.** The plane of a crystal along which it is most readily attacked by chemical action. Often seen on polished and etched surfaces of metals.

**Sorbite.** One of the constituents of steel. It forms the transition stage between troostite and pearlite. Or it may be unsegregated pearlite.

**Spherulitic structure.** Concretionary arrangement often seen in eutectics by quick cooling, resulting from incipient crystallisation. The spherulites often have an internal radiate structure.

**Stellate.** Occurring in star-like forms.

**Surfusion.** The liquid state at temperatures below the normal freezing state.

**Temper.** An expression for the quantity of carbon present in steel. Also used to signify the degree of tempering by reheating hardened steel to a certain temperature. Also used to signify the degree of initial hardness as well as final hardness in steel.

**Temper carbon.** See carbon.

**Tempering.** Modifying the hardness of hardened steel by reheating and judged by the colours generated on the surface by oxidation.

**Troostite.** A constituent of steel, and an intermediate form between martensite and pearlite.

**Vesicular.** Containing small holes.

# INDEX.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